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EVALUATION OF $I_p\,(n-r,\,r+1)$.

By S. R. Savur.

(From the Meteorological Office, Poona.)

Received July 5, 1937.

The function $I_p\,(n-r,\,r+1)$ considered in this note is an incomplete β-function ratio written after the manner of K. Pearson.(1) We will assume here that both n and r are positive integers.

This function can be evaluated using the tables in (1) when both $n-r$ and $r+1$ are not greater than 50. For higher values we may use one of the very approximate methods suggested by Burton H. Camp (2). A defect in these methods is that they do not give us even an approximate magnitude of the error in the value obtained. Hence the method given below may be found to be more useful as it not only gives us this information but also shows us how to increase the accuracy of our result.

We will assume, without loss in generality, that $n-r$ is not less than np.*

$$I_p\,(n-r,r+1) = \frac{n!\,p^{n-r}\,q^r}{(n-r)!\,r!} + \frac{n!\,p^{n-r+1}\,q^{r-1}}{(n-r+1)!\,(r-1)!} + \cdots + p^n.$$

$$= \frac{n!\,p^{n-r}\,q^r}{(n-r)!\,r!}\left\{1 + \frac{r}{(n-r+1)}\cdot\frac{p}{q} + \cdots + \frac{r!}{(n-r+1)\,(n-r+2)\cdots n}\left(\frac{p}{q}\right)^r\right\}$$

$$= U_r \cdot T_1 \qquad \text{(I)},$$

where $q = 1-p$, $U_r = n!\,p^{n-r}\,q^r/\{(n-r)!\,r!\}$,

and T_1 = the series in the curled brackets. Since $n-r \not< np$ we see that $rp/\{(n-r+1)\,q\}$ is less than unity. Hence the series T_1 is monotonous and decreasing. We will assume that r is bigger than say 20. If not, the few terms in T_1 can be summed up directly.

Put $a = p/q$. Then

$$T_1 = 1 + \frac{ra}{(n-r+1)} + \frac{r\,(r-1)\,a^2}{(n-r+1)\,(n-r+2)} + \cdots$$

$$aT_1 = \qquad\qquad a + \frac{ra^2}{n-r+1} + \cdots$$

* For, if $n-r$ be less than np we can write $1 - I_p\,(n-r,\,r+1) = I_q\,(r+1,\,n-r)$, where $q = 1-p$ and then evaluate $I_q\,(r+1,\,n-r)$ for then $r+1$ will be greater than nq.

Adding,

$$T_1(1+a) = 1 + \frac{(n+1)\,a}{(n-r+1)} + \frac{r\,(n+1)\,a^2}{(n-r+1)\,(n-r+2)} + \frac{r\,(r-1)\,(n+1)\,a^3}{(n-r+1)\,(n-r+2)\,(n-r+3)} + \cdots$$

$$= 1 + \frac{(n+1)\,a}{(n-r+1)}\left\{1 + \frac{ra}{(n-r+2)} + \frac{r\,(r-1)\,a^2}{(n-r+2)\,(n-r+3)} + \cdots + \frac{r\,(r-1)\cdots 2\,a^{r-1}}{(n-r+2)\,(n-r+3)\cdots n}\right\}$$

$$= 1 + \frac{(n+1)\,a}{(n-r+1)}\,T_2, \text{ say} \qquad \text{II } (a).$$

Here we have neglected the exceedingly small term $r!\,a^{r+1}/\{(n-r+1)\,(n-r+2)\cdots n\}$.

First Approximation.

Now,

$$T_1 = 1 + \frac{ra}{(n-r+1)} + \cdots + \frac{r\,(r-1)\cdots 2\,a^{r-1}}{(n-r+1)\,(n-r+2)\cdots(n-1)} + \frac{r!\,a^r}{(n-r+1)\,(n-r+2)\cdots n},$$

and $$T_2 = 1 + \frac{ra}{n-r+2} + \cdots + \frac{r\,(r-1)\cdots 2\,a^{r-1}}{(n-r+2)\,(n-r+3)\cdots n}.$$

$$\therefore T_1 - T_2 = \frac{ra\cdot 1}{(n-r+1)\,(n-r+2)} + \frac{r\,(r-1)a^2\cdot 2}{(n-r+1)\,(n-r+2)\,(n-r+3)} + \cdots + \frac{r\,(r-1)\cdots 2\,a^{r-1}\,(r-1)}{(n-r+1)\,(n-r+2)\cdots n}.$$

$$= \frac{ra}{(n-r+1)\,(n-r+2)}\left\{1 + \frac{(r-1)\,a\cdot 2}{(n-r+3)} + \cdots + \frac{(r-1)\,(r-2)\cdots 2\,a^{r-2}\,(r-1)}{(n-r+3)\,(n-r+4)\cdots n}\right\}$$

$$= G_1, \text{ say} \qquad \text{III } (a).$$

Again, we have neglected the very small term

$$r!\,a^r/\{(n-r+1)\,(n-r+2)\cdots n\}.$$

Hereafter it will be taken for granted that whenever any terms are neglected in a similar manner, these terms will be too small to affect our results appreciably. Besides, the places at which such terms are neglected will be so apparent that it will not be even necessary to state where such terms have been left out.

Eliminating T_2 between II (*a*) and III (*a*) and after some reduction we get

$$T_1 = \frac{(n-r+1) - (n+1)\, a\, G_1}{(n-r+1-ar)} \qquad \text{(i)}$$

consider the series G_1' where

$$G_1' = \frac{ra}{(n-r+1)\,(n-r+2)} \left\{1 + 2d_1 + 3d_1^2 + \cdots + (r-1)\, d_1^{r-2}\right\},$$

and $d_1 = (r-1)a/(n-r+3)$.

The first two terms of G_1' are equal to the first two terms of G_1, while all the other terms of G_1' are greater than the corresponding terms of G_1.

$\therefore$ G_1' is greater than G_1.

If we take the series

$$G_1'' = \frac{ra}{(n-r+1)\,(n-r+2)} \left\{1 + 2e_1 + 3e_1^2 + \cdots + (r-1)\, e_1^{r-2}\right\},$$

where $$e_1 = a \left\{\frac{(r-1)\,(r-2)\cdots 2}{(n-r+3)\,(n-r+4)\cdots n}\right\}^{\frac{1}{r-2}},$$

the first and the last terms of G_1'' are respectively equal to the first and the last terms of G_1, while all the other terms of G_1'' are less than the corresponding terms of G_1. Therefore G_1'' is less than G_1. That is,

$$G_1'' < G_1 < G_1'.$$

G_1'' and G_1' can be evaluated since they are respectively equal to $(1-e_1)^{-2}$ and $(1-d_1)^{-2}$.

If we substitute these two values successively in (i) we get two values of T_1 which are one on each side of its true value.

When these two approximations for T_1 are used in equation I we get two values I_1^i and I_2^i one on each side of the true value of I_p $(n-r, r+1)$.

We take $(I_1^i + I_2^i)/2$ as an approximation to the true value. If $I_2^i < I_1^i$ we see that the error in our approximation is less than 50 $(I_1^i - I_2^i)/I_2^i$ %.

$(I_1^i + I_2^i)/2$ is our first approximate value.

Second Approximation.

Corresponding to II (*a*) we get

$$T_2\,(1+a) = 1 + \frac{(n+2)\,a}{(n-r+2)}\, T_3 \qquad \text{II (}b\text{)},$$

where $$T_3 = 1 + \frac{ra}{(n-r+3)} + \frac{r\,(r-1)\,a^2}{(n-r+3)\,(n-r+4)} + \cdots + \frac{r\,(r-1)\cdots 3\cdot a^{r-2}}{(n-r+3)\,(n-r+4)\cdots n}.$$

$$\therefore \quad T_2 - T_3 = \frac{ra}{(n-r+2)(n-r+3)} \left\{ 1 + \frac{(r-1)\,a \cdot 1}{(n-r+4)} + \cdots \right.$$

$$\left. + \frac{(r-1)(r-2)\cdots 3\, a^{r-3}(r-2)}{(n-r+u)(n-r+5)\cdots n} \right\} \qquad \text{III } (b)$$

Subtracting III (b) from III (a) we have

$$T_1 - 2T_2 + T_3 = \frac{ra}{(n-r+1)(n-r+2)(n-r+3)} \times$$

$$\times \left\{ 1 \cdot 2 + \frac{(r-1)\,a\,2 \cdot 3}{(n-r+4)} + \cdots + \frac{(r-1)(r-2)\cdots 3\, a^{r-3}(r-2)(r-1)}{(n-r+4)(n-r+5)\cdots n} \right\}$$

$$= G_2, \text{ say} \qquad \text{IV } (a).$$

Eliminating T_2 and T_3 between II (a), II (b) and IV (a), we obtain

$$T_1 = \frac{(n-r+1)\,\alpha + (n+1)(n-r+2)\,a + (n+1)(n+2)\,a^2 G_2}{(n-r+1)(n+1)\,\alpha + (n+1)(n+2)\,a^2} \qquad \text{(ii)},$$

where $\alpha = (n-r+2)(1+a) - 2(n+2)$.

We also get $G_2'' < G_2 < G_2'$ where

$$G_2'' = \frac{2!\,k_2}{(1-e_2)^3},\ G_2' = \frac{2!\,k_2}{(1-d_2)^3},\ k_2 = \frac{ra}{(n-r+1)(n-r+2)(n-r+3)},$$

$$e_2 = a \left\{ \frac{(r-1)!\,(n-r+3)!}{2!\,n!} \right\}^{\frac{1}{r-3}}, \text{ and } d_2 = \frac{(r-1)\,a}{n-r+4}.$$

Substituting G_2'' and G_2' successively in (ii) we get two new approximations to the true value T_1, and using these two approximations in equation I we obtain two approximations I_1^{ii} and I_2^{ii} to the true value $I_p\,(n-r, r+1)$.

Our second approximation is $(I_1^{ii} + I_2^{ii})/2$. It is easy to see that this approximation is better than the first.

Third Approximation.

In the manner similar to that detailed above we get

$$T_3(1+a) = 1 + \frac{(n+3)\,a}{(n-r+3)}\, T_4 \qquad \text{II } (c),$$

where $T_4 = 1 + \dfrac{ra}{n-r+4} + \dfrac{r(r-1)\,a^2}{(n-r+4)(n-r+5)} + \cdots$

$$+ \frac{r(r-1)\cdots 4a^{r-3}}{(n-r+4)(n-r+5)\cdots n}.$$

and $T_1 - 3T_2 + 3T_3 - T_4 = G_3$ IV (b),

where

$$G_3 = k_3 \left\{ 1\cdot2\cdot3 + 2\cdot3\cdot4\ \frac{(r-1)\,a}{(n-r+5)} + 3\cdot4\cdot5\ \frac{(r-1)\,(r-2)\,a^2}{(n-r+5)\,(n-r+6)} + \cdots \right.$$
$$\left. + (r-3)\,(r-2)\,(r-1)\ \frac{(r-1)\,(r-2)\cdots 4\ a^{r-4}}{(n-r+5)\,(n-r+6)\cdots n} \right\},$$

and $k_3 = \dfrac{ra}{(n-r+1)\,(n-r+2)\,(n-r+3)}$.

Eliminating T_2, T_3 and T_4 from II (*a*), II (*b*), II (*c*) and IV (*b*), we get

$$T_1 = \frac{(n-r+1)\beta_2 + (n+1)(n-r+2)a\beta_1 + (n+1)(n+2)(n-r+3)a^2 - (n+1)(n+2)(n+3)a^3 G_3}{(1+a)\,(n-r+1)\,\beta_2 - (n+1)\,(n+2)\,(n+3)\,a^3} \qquad \text{(iii)},$$

where $\beta_2 = (1+a)\,(n-r+2)\,\beta_1 + 3\,(n+2)\,(n+3)\,a^2$, and

$\beta_1 = (1+a)\,(n-r+3) - 3\,(n+3)\,a$.

The two approximations to G_3 are $G_3'' < G < G_3'$,

where $G_3'' = k_3 \dfrac{3!}{(1-e_3)^4}$, $G_3' = k_3 \dfrac{3!}{(1-d_3)^4}$,

$$e_3 = a \left\{ \frac{(r-1)!}{3!}\ \frac{(n-r+4)!}{n!} \right\}^{\frac{1}{r-4}} \text{ and } d_3 = \frac{(r-1)\,a}{(n-r+5)}.$$

These enable us to get a better approximation to I_p $(n-r,\ r+1)$ than our second approximation.

Higher Approximations.

The method of getting closer and closer approximations is now clear. We will content ourselves by merely giving the result in the *c*th approximation. Proceeding as before we get,

$$T_1 = \frac{\begin{array}{l}(n-r+1)\,\gamma_{c-1} + (n+1)\,(n-r+2)\,a\,\gamma_{c-2} + (n+1)\,(n+2)\times \\ \times(n-r+3)\,a^2\,\gamma_{c-3} + \cdots + (n+1)\,(n+2)\cdots(n+c-2)\,(n-r+c-1)\,a^{c-2}\,\gamma_1 \\ +(n+1)(n+2)\cdots(n+c-1)\,(n-r+c)\,a^{c-1}\end{array}(-)^c\,(n+1)\,(n+2)\cdots(n+c)\,a^c G_c}{(1+a)\,(n-r+1)\,\gamma_{c-1}\,(-1)^c\,(n+1)\,(n+2)\cdots(n+c)\,a^c}$$

where

$$G_c = k_c \left\{ 1\cdot2\cdot3\cdot\cdot c + 2\cdot3\cdot4\cdot\cdot(c+1)\,\frac{(r-1)\,a}{(n-r+c+2)} + \cdots \right\},$$

$$k_c = \frac{ra}{(n-r+1)\,(n-r+2)\cdots(n-r+c+1)},$$

$$\gamma_{c-1} = (1+a)\,(n-r+2)\,\gamma_{c-2}\,(-)^{c-1}{}_cC_1\,(n+2)\,(n+3)\cdot\cdot(n+c)\,a^{c-1},$$

$$\gamma_{c-2} = (1+a)(n-r+3)\,\gamma_{c-3} - {}_cC_2\,(n+3)(n+4)\cdots(n+c)\,a^{c-2},$$

.....

$$\gamma_1 = (1+a)(n-r+c) - c\,(n+c)\,a.$$

The two approximations to G_c are

$$G_c'' < G_c < G_c', \text{ where}$$

$$G_c'' = k_c \frac{c!}{(1-e_c)^{c+1}},\ e_c = a\left\{\frac{r!\,(n-r+c+1)!}{c!\qquad n!}\right\}^{\frac{1}{r-c-1}},$$

$$G_c' = k_c \frac{c!}{(1-d_c)^{c+1}} \text{ and } d_c = \frac{(r+1)\,a}{(n-r+c+2)}.$$

These enable us to get the cth approximation to $I_p\,(n-r,\ r+1)$.

It is easy to see that there is a limit to which the approximation can be pushed by this method, this limit depending upon the terms neglected by us. We can, however, overcome this defect by introducing correction terms which take into account the terms left out. The method of working out these correction terms is quite simple and so it is not given here. The total correction to T_1 is also not given as its literal expression is somewhat cumbersome.

However, at any stage we can find out approximately whether the error due to the neglect of the terms is less than the difference between the two relevant approximations obtained by our method. If so, it will not be necessary to work out the correction at all. We can proceed as follows.

The equations for the cth approximation, neglecting none of the terms, are

$$T_1 = \frac{1}{1+a} + \frac{(n+1)\,a}{(n-r+1)\,(1+a)}\,T_2 + \frac{a}{1+a}\,\delta_1 \qquad (1),$$

$$T_2 = \frac{1}{1+a} + \frac{(n+2)\,a}{(n-r+2)\,(1+a)}\,T_3 + \frac{a}{1+a}\,\delta_2 \qquad (2),$$

.....

.....

$$T_c = \frac{1}{1+a} + \frac{(n+c)\,a}{(n-r+c)\,(1+a)}\,T_{c+1} + \frac{a}{1+a}\,\delta_c \qquad (c)$$

and $T_1 - {}_cC_1T_2 + {}_cC_2T_3 \cdots (-)^cT_{c+1} = G_c + \delta_1 - {}_{c-1}C_1\delta_2 + {}_{c-1}C_2\delta_3 - \cdots (-)^{c-1}\,\delta_c$..... $(c+1)$,

where $$\delta_m = \frac{r!\,(n-r+m-1)!\,a^{r-m+1}}{(m-1)!\,n!}.$$

Now, c is small compared with $n - r$. Hence the correction terms, $\delta_1, {}_{c-1}C_1\ \delta_2, \cdots$ on the r.h. of $(c + 1)$ are in the ascending order of magnitude. Thus the total of the correction terms in equation $(c + 1)$ above is numerically less than δ_c.

Again, $a = p/q < (n - r)/r$. Hence the coefficient of T_{k+1} in the kth equation above is

$$\frac{(n + k)\ a}{(n - r + k)\ (1 + a)} < \frac{(n + k)\frac{n-r}{r}}{(n - r + k)\left(1 + \frac{n - r}{r}\right)} = \frac{(n+k)\ \ (n-r)}{(n - r + k)\ n} < 1.$$

For working out an approximate value of the total correction to T_1 we may replace the coefficient of the T's on the r.h. of equations (1) to (c) by unity, each of $\delta_1, \delta_2, \cdots$ by δ_c, and the total of the correction terms of $(c + 1)$ by $\pm\ \delta_c$, that sign being retained which gives a positive sign to this term in the total correction to T_1. We now see that the correction to T_1 in the cth approximation is less than $[1 + ca/(1 + a)]\ \delta_c$.

We will apply this method to one of the examples worked out by Camp. Let us take example (1) on page 166 of (2). The results are given below.

Order of Approximation	I_1 $\times 10^{-5}$	I_2 $\times 10^{-5}$	$\frac{1}{2}(I_1 + I_2)$ $\times 10^{-5}$	Maximum error in $\frac{1}{2}(I_1 + I_2)$ %
First ..	5·32	5·14	5·24	1·6
Second ..	5·170	5·148	5·159	0·22
Third ..	5·1683	5·1651	5·1667	0·031
Fourth ..	5·1662	5·1656	5·1659	0·0058
Fifth ..	5·16604	5·16598	5·16601	0·00058

The error in the fifth approximation due to the neglected terms is less than $3 \cdot 2 \times 10^{-201}$ and is therefore quite negligible.

If we go down the column $\frac{1}{2}(I_1 + I_2)$ we see that the successive approximations are alternately greater and less than the true value. From the manner in which the error has been getting continually diminished we can see that the sixth approximation is $5 \cdot 16601 \times 10^{-5}$. Hence the true value is $5 \cdot 16601 \times 10^{-5}$ correct to the fifth decimal place.

The approximate value obtained by Camp using his equation (ix) on page 166 of (2) is $5 \cdot 1659 \times 10^{-5}$ which is an error by unity in the last decimal place. Camp gives the true value as $5 \cdot 1662 \times 10^{-5}$. This value appears to be in error in the 4th decimal place as the five approximations given in the above table have been verified independently.

In conclusion, I wish to thank Messrs. D. Sankaranarayan and L. S. Mahalingam, of the Statistical Section, the India Meteorological Department, for having kindly verified some of the results obtained in this paper.

Summary.

A method of evaluating $I_p\ (n - r, r + 1)$ approximately is described. This method enables us to obtain closer and closer approximations and also to find out an upper limit to the error in any of these approximations.

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AN ENERGETICAL INTERPRETATION OF THE SEMIPOLAR DOUBLE BOND.

By R. Samuel.

Received September 11, 1937.

Absorption spectra of inorganic nitrates in the vapour state have been investigated simultaneously by Butkow and Tschassowenny[1] and by Haq and Samuel[2] with almost identical experimental procedures and results. There is little doubt about the covalent nature of the metal-oxygen bond of these compounds in the vapour state, and the transition to electrovalency in solution, as pointed out elsewhere,[3] is due to the additional energy of hydration.

There appears to be, however, a difference of opinion as to the character of the second N = O bond of the nitro-group. Butkow and Tschassowenny interpret their results by means of the semi-polar double bond, introduced by Sidgwick a.o.,[4] whereas we consider the same experimental results as a further argument against the existence of such co-ordinate linkages in simple inorganic molecules of first order. In the following we give therefore an energetical interpretation of this phenomenon based on a number of experiments on the photo-dissociation of inorganic molecules.[5] It retains, we believe, the essential features of this conception as far as chemical reactivity is concerned, without introducing a second variety of covalency for such molecules.

In the case of the nitro-group some difficulties occur on account of the inaccuracy and the lack of certain thermochemical figures. Hence we begin with the exactly similar example of the sulphates and sulphites and consider first the formation of the SO_2 and SO_3 molecules. The bonds in SO and SO_2 are very nearly related to each other. The dissociation energy of SO taken from its band spectrum[6] is 5·05 e.v., the atomic energy of formation* of SO_2 is 246·4 k.cal./mol. = 10·7 e.v. which is almost precisely double the former value. Furthermore, the analysis of the near ultra-violet SO_2 bands[7] shows, that the energy of excitation and the symmetric valence vibration of the excited and unexcited state are almost identical with the corresponding

* The thermochemical figures and calculations are the same as in the preceding papers.[5,7] Some figures are slightly changed on accouut of the data of K. K. Kelley's new survey on the "Free Energies of Vaporization and Vapour Pressures of Inorganic Substances" (Bureau of Mines, U. S. Dept. of the Interior, Washington, 1935).

values of the SO molecule. Moreover, a large number of investigations of the absorption spectra of halides and oxyhalides of S, Se and Te have shown that the energy of bonds such as S = O, S = S, Se = O, Se = Se, S – Cl, S – Br, Se – Cl, Se – Br, etc., remain almost unchanged in such widely different molecules as SO, $SOCl_2$, $SOBr_2$, S_2, SCl_2, S_2Cl_2, SeO, Se_2, SeO_2, $SeOCl_2$, Se_2Cl_2, $SeCl_4$, etc.

In all these molecules the central atom is in the di- or tetravalent state. For molecules such as SO_3, SO_2Cl_2, etc., involving hexavalency of the central atom, the law of approximate additivity of the bond energies at the first glance appears not to hold good. The atomic energy of formations of SO_3 is 325·6 k.cal./mol. = 14·1 e.v. which is distinctly lower than three times D (SO) and in other cases, *e.g.*, PCl_3 and PCl_5, etc., the disagreement is even much larger.

The explanation is quite simple. The formation of SO_3 is not brought about by the combination of unexcited SO_2 in its ground state $^1\Sigma$ *plus* unexcited oxygen atoms in the ^3P term. The electronic configuration of the sulphur atom is $3s^23p^4$ and its di- and tetravalent state involve unexcited sulphur atoms. To make sulphur hexavalent an excitation to a $3s3p^5$ term is indispensable because the completed group $3s^2$ does not possess bonding power, but acts repulsively only.† This view of the Heitler-London pair bond theory of valency has been supported by direct spectroscopical evidence.[8] The ground level of SO_3 therefore does not belong to the same series as those of the SO and SO_2 molecules. The normal states of these later compounds are formed by combination of unexcited atoms and molecules, whereas the adiabatic dissociation of unexcited SO_3 involves excited products. Experimentally this is quite certain, as both molecules SO_2 and SO_3 are diamagnetic, which a molecule formed by the combination of SO_2 ($^1\Sigma$) *plus* O (^3P) could not be. All spin vectors being counterbalanced already in the singlet level of SO_2, there are no free vectors left to neutralise those of the triplet term of oxygen to yield a singled term of SO_3.

The relative position of the ground states of the three molecules is shown in the simplified Franck-Condon Diagram of Fig. 1 of the system S + 3O. The approach of unexcited O atoms towards the unexcited S atom or the unexcited SO molecule leads to the formation of SO and SO_2 molecules. But on the approach of unexcited O atoms towards unexcited SO_2 no chemical union but an elastic collision takes place. This is represented in

† A more detailed discussion on the electronic configurations of the atoms and their valencies in polyatomic molecules will be found in a forthcoming paper by Lessheim and Samuel.

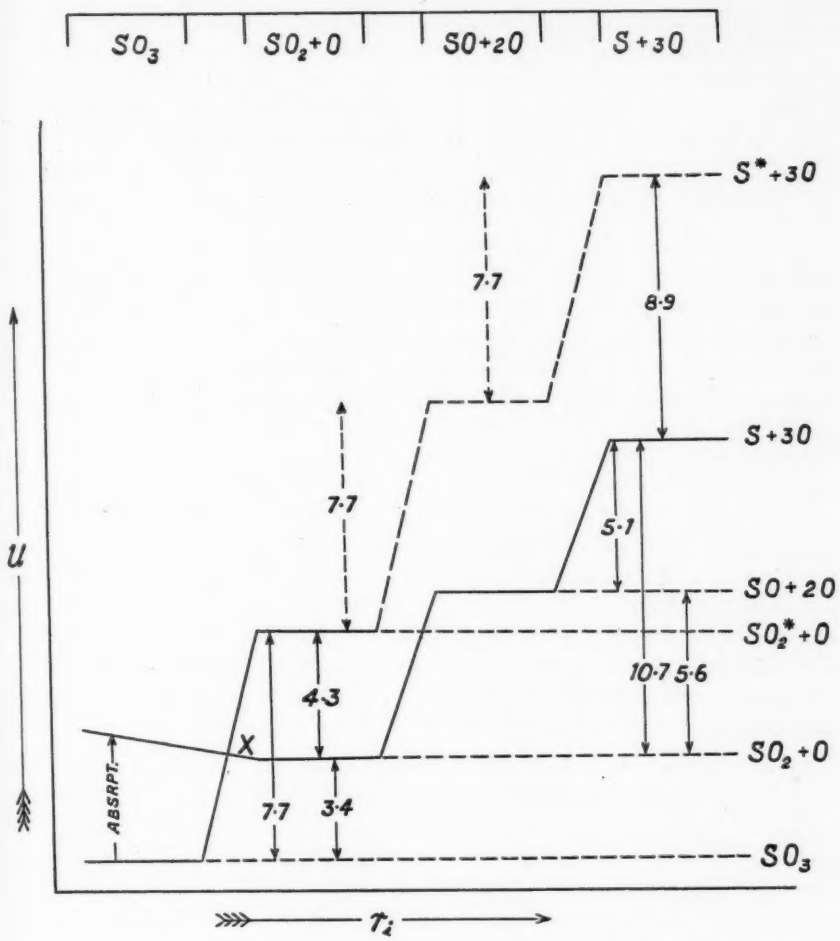

FIG. 1.

the diagram by a repulsive curve without a stable minimum. The products of adiabatic dissociation of SO_3 most certainly are either $SO_2 + O^*$ or SO_2^* *plus* O and no direct experimental evidence exists at present which permits to decide between these two possibilities. Theoretically, however, chemical union is not possible unless the original s^2 group is split previously. Therefore in the diagram the ground level of SO_3 is connected with a level involving an excited SO_2 molecule. The energetic position of this level can be estimated. The adiabatic dissociation of this state finally involves a sulphur

atom in the $3s3p^5$ configuration. The known state $3s3p^5\ ^3P$ appears to be identical with the lowest term of this configuration. It has an energy of excitation of 8·9 e.v. which added to D (SO_3) = 14·1 e.v. yields a value of 23·0 e.v. for the adiabatic energy of dissociation of SO_3 into $S^* + 3O$. For the mean bond energy D_B ($S^{VI} = O$) taken as one-third of this figure, 7·7 e.v. obtains. The term of excited SO_2 therefore lies approximately 7·7 e.v. above the ground level of SO_3 or 4·3 e.v. above that of SO_2.

The existence of the repulsive potential curve SO_2 ($^1\Sigma$) + O (^3P) is indicated by the absorption spectrum. The long wave limit of continuous absorption has been measured by various authors[9] and lies at an energy value of about 80 to 85 k.cal./mol., slight differences being accounted for by the experimental difficulty to determine the value associated with the lowest state of vibration. This result therefore agrees very well with the energy difference D (SO_3) − D (SO_2) = 81·2 k.cal./mol. Kornfeld directly used the SO_2 absorption bands as an indicator of the photo-dissociation of SO_3. Moreover, Dutta found the beginning of the second region of selective absorption at 124 k.cal./mol. The difference between the two long wave limits agrees with the excitation energy of the ^1D term of O = 1·96 e.v. = 45·1 k.cal./mol.‡ Similarly, the long wave limit of the continuous absorption spectrum of TeO_3 lies at 62·1 k.cal./mol.[10] and agrees with the thermochemical energy difference D (TeO_3) − D (TeO_2) ~ 53 k.cal./mol. Again that of SO_2Cl_2 at 108·6 k.cal./mol. agrees with the value D (SO_2Cl_2) − D ($SOCl_2$) = 110·0 and pyrosulphuryl chloride $S_2O_5Cl_2$ shows a long wave limit of almost the same value, *i.e.*, 113 k.cal./mol.[5]

For molecules of a *lower* state of valency of the central atom of the types PCl_3, SCl_2, $SeCl_4$ the first red wave limit always agrees with the bond energy and the products of photo-dissociation are unexcited atoms and radicals possessing free valencies.[5,11] But the photolytic dissociation of such simple molecules formed by atoms in their state of *maximal* valency produces not radicals, but unexcited atoms and saturated molecules of lesser valency of the central atom; the red wave limit always agrees with the thermochemical difference of the atomic energies of formation of these two molecules. Just this difference of behaviour clearly indicates that in a molecule formed by hexavalent sulphur such as SO_3 the absorption of light corresponds to a transition from the ground level of the molecule to the repulsive

‡ Some difficulties experienced in the interpretation of the absorption spectra of SO_3, etc., disappear on the replacement of the value of $D(S_2) = 4.4$ e.v. taken from predissociation data, by the new value of 3·8 e.v. calculated directly from the convergence point. (R. K. Asundi and R. Samuel, *Proc. Phys. Soc. Lond.*, 1936, **48**, 28; *Proc. Ind. Acad. Sci.*, 1936, **3**, 466.)

curve SO_2 ($^1\Sigma$) *plus* O (^3P), while an attractive curve involving these products does not exist.

The position of the binding level $SO_2^* + O$ 4·3 e.v. above the ground level of SO_3 is interesting also from another point of view. The origin of the near ultra-violet absorption bands has been located at 33303 cm.$^{-1}$ = 4·1 e.v.[7] The appearance of the bands and the vibrational frequencies obtained make it difficult to identify the upper level of these bands with that term in which the s^2 orbital has been fissured. But Franck, Sponer and Teller[12] have shown that the pseudo-predisssociation of these bands is due to perturbations owing to the existence of another electronic level in the immediate vicinity of the first one. The close agreement of the above figures derived in an entirely different way makes it probable that this disturbing term is indeed the excited level of SO_2 involved in the adiabatic dissociation of SO_3.

These considerations may be summed up as follows :—

The energy difference (3·4 e.v.) between the ground level of a molecule whose central atom exhibits its maximal valency (SO_3) and the corresponding molecule of lesser valency of the central atom (SO_2) is less than the bond energy of the latter (5·4 e.v.) and much less than that of the former (7·7 e.v.). For chemical reactions, however, not the bond energies but their actual differences are decisive. For all practical purposes the oxidation of SO_2 may be described in the following way :—On the approach of unexcited oxygen atoms to unexcited SO_2 molecules the system will follow the repulsive curve with a small amount of energy of activation until the point of intersection (X in the diagram) with the potential curve of the ground level of SO_3 is gained. The thermochemical difference $D_T = D(SO_3) - D(SO_2)$ remains as chemical heat of reaction, whether the D values directly represent the sum of the bond energies or not.

Exactly the same conditions prevail in the corresponding molecules formed by nitrogen, but the calculation of the two bond energies is more difficult and uncertain. It is not permitted to divide, *e.g.*, the atomic heat of formation of N_2O_3 into three equal parts, two of the oxygen atoms being linked by double bonds, one by two single bonds. In the following table the atomic energies of formation D are listed together with the heats of formation Q from which they are derived§ :—

§ With D (N_2) = 169·5, D (O_2) = 116·4 and D(H_2) = 102·7. Q (HNO_2) refers to an aqueous solution, D (HNO_2) will be slightly smaller. Q (N_2O_3) is an older value (*cf.* Mellor, *Comprehensive Treatise*) and possibly not quite accurate.

	NO	NO_2	N_2O_3	N_2O_5	HNO_2	HNO_3	NCl_3	NOCl
Q	−21·6	−8·1	−22	−1·2	(30·8)	34·4	−54·7	−6
D	120·3	193·0	322·1	459·3	<282·3	345·1	117·8	126·9
D_T	73·3		2× 68·6		> 62·8			

The differences D_T of the D values of corresponding molecules formed by tri- and pentavalent nitrogen respectively are about 70 k.cal./mol. and 69 k.cal./mol. have been deduced similarly[2] for ethyl nitrate and ethyl nitrite from their respective heats of combustion. The chemical heat of reaction of the oxidation of the nitroso group will be $D_T = 70$ k.cal./mol. Deducting 1/3D (NCl_3) from D (NOCl) a value of 126·9 k.cal./mol. obtains for the bond energy D_B ($N^{III} = O$) which is quite near to D (NO). Adding the energy of excitation of N ($2s2p^4\,{}^4P$) = 250·7 to D (NO_2), 221·9 obtains for D_B ($N^V = O$). Again the true bond energy, *i.e.*, the energy of adiabatic dissociation, of the state of maximal valency is larger than that of lower valency, whereas the heat of reaction D_T involved in the transition from one to the other is smaller than both.

The conception of the semi-polar double bond as a second kind of covalent linkage has been introduced for various reasons. Leaving aside genuine complex salts[15] and speaking of molecules of first order only, these reasons may be conveniently divided into two classes. One series of arguments has been connected with the Octet Rule. It maintains that the formation of an electron octet confers stability to a molecule. Other arguments are mainly concerned with questions of stability and reactivity.

Considerations of the first kind have been discussed of late from the present point of view in a number of preceding publications.[8] A few words may be sufficient here. The conception of the co-ordinate bond has been introduced in order to obtain a formal formation of an electron octet also in such cases where the central atom exhibits more than four valencies. The nitro-group is a typical example. It has been shown that this conception is contradicted by new band spectroscopical evidence which shows that just the so-called " lone pair " of electrons, the agent of co-ordination, is the completed s^2 group which does not possess bonding power. Furthermore, there does not exist any physico-chemical evidence which proves the existence of a second kind of covalent linkage in molecules of first order.

The covalency exhibited by the nitrates in the vapour state is also worthy of note. It may be recalled that the prevailing influence of octet formation was made apparent by two entirely different classes of molecules, the organic molecules, where it is the outcome of the tetravalency of C, and the simple salts which dissociate in solution into two ions possessing the configuration of the corresponding rare gas. As to the latter ones, the existence as free ions, *i.e.*, the existence of a positive electron affinity of negative ions mainly of group VII, and a low ionisation potential of the metals mainly of groups I and II, is of course due to their neighbourhood to the rare gases in the periodic table and the ease by which they assume their electronic configuration. But the number of valencies exhibited by such atoms is in no way connected with this phenomenon. Under suitable experimental conditions these electrovalent links may turn into ordinary covalent bonds, as has been shown by Franck and his collaborators[13] in the case of silver halides and by Butkow, Oeser and Wieland[14] in that of divalent metals with high ionisation potentials. The absorption spectra of the nitrates and sulphates in the vapour state show that even metals with very low ionisation potentials like Na or K, form covalent molecules if the electron affinity of the partner is sufficiently low. But atoms like K or Mg cannot be assumed to be surrounded by an electron octet in such molecules. Clearly the number of valencies exhibited is quite independent of the possibilities of octet formation and the electrovalent or covalent nature of the bond. As a matter of fact, just these experiments indicate again that numerical valency depends entirely on the number of outside electrons of an atom. It is therefore a property of the free atom quite independent of the partner. The existence of *e.g.*, the five, six, and seven covalent bonds of nitrogen, sulphur and iodine respectively does not constitute a new phenomenon; they do not require any other explanation than the covalent bonds of liquid LiEt or of AgCl vapour, etc., where likewise octet formation does not take place.

The second main argument for the introduction of a co-ordinate bond into the formulæ of such molecules of first order is of an energetical nature. In certain cases the transition from a lower to the maximal state of valency at first sight appears to produce bonds of less stability. A typical example is the reaction $PCl_5 \rightarrow PCl_3 + Cl_2$ which indeed takes place with great ease and appears to indicate a reduced energy of the bonds of the last two chlorine atoms. Other examples are for group IV atoms, *e.g.*, the decomposition of $PbCl_4$ or $SnCl_4$ into $PbCl_2$ or $SnCl_2$ and for group VI the greater

stability of SO_2 as compared with SO_3.$ In all these examples the central atom of the less stable molecule exhibits its maximal valency according to the number of its outside $s + p$ electrons whereas the numerical valency of the central atom of the more stable molecules agrees with the number of the p electrons alone.

As has been seen, the true bond energies in such cases of maximal valency, as *e.g.*, PCl_5, are rather increased, because the adiabatic dissociation of such a molecule involves an excited P atom, the s^2 group of electrons being split. The high reactivity is due to the low value of $D_T = D(PCl_5) - D(PCl_3)$ brought about by the beginning at an excited level of the adiabatic formation of the molecule. This places the ground level of PCl_5 at a level lower than that of PCl_3 but not as low as it would be otherwise. The corresponding figures are 3·4 and 5·4 e.v. for SO_3 and SO_2 respectively, but only the latter value represents a true bond energy.

The increased reactivity and the ease of such reactions, to our mind, are not an indication of a second variety of covalent linkage, *i.e.*, of a bond of lesser energy. They are brought about by the lack of free valencies of the molecules of lesser numerical valency. Further chemical combination takes place only after an excitation of this molecule involving a splitting of the original s^2 group of the central atom. An increased energy of adiabatic *dissociation* results always, but in certain cases the energy *difference* of the ground levels of the two molecules is considerably decreased and if the bond energies are not very great (as probably in SF_6) an increased reactivity results. Essentially, this is due to the non-bonding and repulsive character of the s^2 group in accordance with the Heitler-London pair bond theory of valency.

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RÔLE OF ARGON IN THE PRODUCTION OF SWAN BANDS.

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I. Introduction.

In a discharge tube, generally three factors affect the distribution of intensity among the lines of a spectrum. These three factors are :—(i) electrical conditions of excitation, (ii) the pressure of the gas in the discharge tube and (iii) the presence of impurities. Nature of changes in the distribution of intensity due to these factors is the selective transfer of energy from higher term members to lower term members of the series. The presence of the foreign gas in a discharge tube plays an important part, the effects due to this being quite different from those due to the electrical conditions of excitation and the pressure of the gas.

It has been shown in several papers that an admixture of the inactive gas with substances emitting spectra results, in certain cases, in profound modification of these spectra. In some cases, this is in the form of redistribution of spectral intensity, but in others, an isolation of spectra entirely new, is effected. Remarkable results of this kind have been obtained by Merton[1] while working with helium. This includes, a redistribution of intensity in the secondary spectrum of hydrogen and under other conditions, a peculiar facility in isolating higher term members of the Balmer series of hydrogen. In connection with carbon, helium favours the production of certain spectra, appropriate to extremely low pressures and with other spectra, effects an isolation, otherwise difficult or impossible. Various authors have studied the effects of foreign gases, like helium, argon and neon on spectra of many substances, such as hydrogen, carbon, oxygen, nitrogen, sulphur and many others. In view of this work, it occurred to us to study certain aspects of the isolation of spectra under the influence of foreign gases. In particular, there are various spectra associated with carbon. In this connection, we can point out the different band systems attributed to carbon which occur with the change in condition of excitation or change of pressure or in the presence of certain foreign gases. Johnson[2] has shown that in a discharge tube of "H" pattern having a capillary and fitted with carbon electrodes, green light of exceptional brilliance is emitted, if the tube be filled with argon at a pressure of about 30 mm. This stage comes only when the tube is in the right condition. The presence or absence of hydrogen has a marked effect on the

emission of this light which is due to Swan system. In order to follow this effect of high pressure argon on the isolation of Swan system, we propose to make a systematic study of the intensity changes that take place in the Swan system by the gradual addition of argon to the discharge tube of the type indicated above. The necessity of such an investigation has been pointed out already, by Johnson and Tawde.[4] We shall confine our investigations to only five different pressures (namely 10, 15, 20, 25 and 30 mm.) of argon.

II. Experimental.

The Swan bands were excited in discharge tubes filled with argon at different pressures. Such tubes were of the usual "H" pattern having one carbon electrode and one aluminium electrode. The light was examined through the spectroscope by focussing a capillary portion on the slit. The capillary was about 20 cm. in length and 1·5 mm. in diameter. Two small bulbs containing P_2O_5 and KOH were attached to the discharge tube. The palladium regulator was also attached to admit or remove hydrogen from the tube. Spectrally pure argon obtained in small glass cylinder from the British Oxygen Co., Wembley, was used for these experiments. Pressures were measured by a mercury manometer attached to the tube. It was necessary to use liquid-air trap to catch mercury vapours from the manometer diffusing in the discharge tube, as it is known that the argon at high pressure, tremendously enhances the arc spectrum of mercury. The liquid-air trap minimises the trouble to a great extent, though it does not completely remove the mercury vapours. This was evident from the slight traces of intense mercury lines found in the spectrum. The tubes were filled at required pressures (namely 10, 15, 20, 25 and 30 mm.) respectively, sealed and taken for photographing the spectrum, as required. Before doing that, the palladium regulator attached to the tube was heated for a sufficiently long time to remove hydrogen from the tube. This can be done easily when the regulator is heated in the very tip of a Bunsen flame. When hydrogen is completely removed the tube showed only Swan bands and almost negligible traces of intense mercury lines.

In the work of this type where the investigations are concerned with the vibrational intensities, a moderately low dispersion instrument was necessary. So the spectrum was photographed on a Hilger constant deviation spectrograph having dispersion of about 70 Å.U. per mm. at λ 6000 and about 20 Å.U. at λ 3000. The slit of the spectrograph was adjusted to a value which just made the fine structure of bands to disappear leaving the band structure almost a continuous spectrum. The spectrum was photographed by focussing on the slit of the spectrograph, a sharp image of the capillary nearer the carbon electrode by means of a condensing lens.

The discharge was run by a large induction coil giving a high-frequency voltage discharge, no condenser or spark gap being used in the circuit. The primary voltage was 18 volts and with it, the current in the secondary was 50 milliamps maintained fairly constant throughout the work.

Ilford Rapid Process Panchromatic Plates (backed ones) were used. On each plate, two sets of spectra and calibration marks were taken, one set being for a group of strong bands and the other for a slightly weaker group. For the correlation of intensities of bands from one set to another, bands of intermediate intensities were kept common to both the sets. The spectrum was photographed alongside a set of calibration marks due to a standard lamp. For this, a step-slit having six slits of widths, 0·198; 0·296; 0·471; 0·723; 1·326 and 2·098 mm. was used. These widths of the slits were so selected that the minimum was such as not to cause any diffraction effects and the maximum was just sufficient to avoid extraneous light filling the spectrograph. This step-slit was illuminated by a standard lamp of known energy distribution. In order to produce uniform illumination over all the slits of the step-slit, the lamp was accurately placed in line with the axis of the collimator tube, at a sufficiently long distance, no lens being used. The lamp used was a special U.V. glass tungsten spiral filament lamp supplied by the General Electric Company. During the time of exposure, the value of the current in the lamp was maintained at a fixed value of 1·9 amperes by means of a rheostat in the circuit, as the lamp was calibrated at that value of the current. The calibration of the lamp used in this work, was carried out by Dr. Johnson and one of us (N.R.T.) at the Government Chemical Laboratories, London, and the data of energy distribution supplied to us through the courtesy of those authors. Times of exposure for the spectrum as well as the calibration marks for the standard lamp were adjusted strictly equal and were such that the spectrum blackening was intermediate between the maximum and minimum of the calibration marks. In case of lamp, intensity being very strong in comparison with that of the spectrum, it was necessary to reduce the lamp intensity. This can be easily done by using neutral filters in front of the lamp and also by varying the distance of the lamp from the slit. Thus it was possible to adjust the exposures strictly equal. The plates were developed and fixed with the usual precaution necessary in such a kind of work. Microphotometering of plates was carried out on a Zeiss self-recording instrument belonging to the Physics Laboratory of the Science College, Patna. For this purpose, two or three plates were selected for each pressure from the several plates taken as above. The instrument was tested for perfect reproducibility by taking a trial record of a spectrum and then running

the spot of light backwards. The record thus obtained should not show any overlapping by another curve. Records were obtained for the required band heads and the calibration marks at the corresponding points.

Records thus obtained enabled the photographic intensities of each band head to be calculated. This was taken corresponding to the peak of each band immediately near the head. They were then expressed in terms of the energy distribution of the standard lamp by means of the calibration curve ($E_\lambda : \lambda$) of the lamp. The details of these have been sufficiently treated by Johnson and Tawde and others.[4, 10]

III. Results of Observations.

(1) *Intensities.*—The results of final intensity values for five different pressures of argon gas are recorded in Table I below. They are expressed on a relative scale, with (0, 0) band at λ 6165 as 100.

TABLE I. *Intensities.*

Bands	Pressure of Argon				
	10 mm.	15 mm.	20 mm.	25 mm.	30 mm.
0, 2	7·08	7·70	5·91	4·79	5·90
1, 3	8·89	15·89	14·12	8·51	9·58
2, 4	6·50	21·15	15·31	9·24	12·49
3, 5	5·13	14·86	10·80	4·98	8·61
4, 6	2·69	10·65	9·25	3·92	6·17
5, 7	1·06	7·89	4·92	2·6	4·35
0, 1	50·60	35·89	41·98	45·98	47·50
1, 2	26·31	32·95	32·75	24·92	25·77
2, 3	17·95	22·10	27·00	17·33	15·16
3, 4	14·71	19·01	21·00	10·29	11·39
4, 5	9·63	11·79	11·43	7·51	5·02
5, 6	5·80	6·85	8·25	4·25	3·20
0, 0	100·0	100·0	100·0	100·0	100·0
1, 1	44·17	61·39	54·03	56·18	47·39
2, 2	12·8	19·79	13·17	13·69	18·48
1, 0	63·47	72·74	65·99	53·55	69·60
2, 1	31·87	62·66	43·95	29·96	33·27
3, 2	24·69	59·17	40·98	24·30	30·19
4, 3	13·95	49·91	29·85	15·93	18·36
5, 4	10·15	38·05	22·16	11·05	15·26
2, 0	17·21	22·71	10·86	14·76	19·01
3, 1	11·52	23·71	12·26	10·18	16·07
4, 2	12·8	30·30	10·98	11·8	20·85

(2) I/ν^4 *Values and Transition Probabilities.*—The values of I/ν^4 have been calculated in order to arrive at transition probabilities and the statistical weights of initial levels. These values are recorded in Tables II, II (*a*) and III. Most probable transitions have been derived for all the

TABLE II.

I/ν^4 *Values.*

Bands	Argon Pressure				
	10 mm.	15 mm.	20 mm.	25 mm.	30 mm.
0, 2	10·38	11·39	8·66	7·02	8·65
1, 3	12·47	22·26	19·79	11·93	13·43
2, 4	8·75	28·46	20·61	12·43	16·81
3, 5	6·65	19·27	14·01	6·46	11·17
4, 6	3·48	13·37	11·61	4·92	7·74
5, 7	1·4	9·63	6·01	3·4	5·4
0, 1	50·91	39·13	42·14	46·25	47·79
1, 2	25·55	31·99	31·79	24·19	25·02
2, 3	16·88	20·78	25·39	16·29	14·23
3, 4	13·45	17·37	19·31	9·41	10·41
4, 5	8·59	10·51	10·19	6·69	4·48
5, 6	5·30	6·5	8·6	4·20	2·30
0, 0	71·00	71·00	71·00	71·00	71·00
1, 1	30·49	42·37	37·29	38·79	32·71
2, 2	8·62	13·32	8·87	9·22	13·44
1, 0	31·85	36·50	33·12	26·87	34·93
2, 1	15·71	30·87	21·65	14·76	16·40
3, 2	11·98	28·71	19·88	11·79	14·65
4, 3	6·68	23·91	14·30	7·63	8·80
5, 4	4·82	18·06	10·52	5·25	7·24
2, 0	6·32	8·34	3·99	5·42	6·98
3, 1	4·19	8·62	4·46	3·70	5·84
4, 2	4·62	10·83	3·96	4·26	7·52

TABLE II (*a*). $\Sigma I/\nu^4$ *Values and Statistical Weights.*

v'' Progression ↓	Argon Pressure				
	10 mm.	15 mm.	20 mm.	25 mm.	30 mm.
$v' = 0$	132·30	121·5	121·80	124·27	127·5
$v' = 1$	100·5	133·2	122·00	101·78	106·0
$v' = 2$	56·3	101·8	80·61	58·12	67·9
$v' = 3$	36·4	74·0	57·67	31·46	42·1
$v' = 4$	23·4	58·6	40·76	23·50	28·4
$v' = 5$	11·52	34·2	24·13	12·85	14·9
Total weight for the system →	357·42	523·3	446·97	351·98	386·8

TABLE III. *Transition Probabilities.*

Bands	Argon Pressure				
	10 mm.	15 mm.	20 mm.	25 mm.	30 mm.
0, 2	0·079	0·094	0·071	0·056	0·068
1, 3	0·124	0·167	0·162	0·117	0·126
2, 4	0·156	0·287	0·256	0·213	0·247
3, 5	0·184	0·261	0·243	0·207	0·266
4, 6	0·150	0·229	0·289	0·208	0·271
5, 7	0·122	0·281	0·249	0·264	0·362
0, 1	0·385	0·322	0·346	0·373	0·375
1, 2	0·255	0·240	0·267	0·238	0·236
2, 3	0·300	0·204	0·315	0·281	0·211
3, 4	0·371	0·235	0·336	0·299	0·247
4, 5	0·368	0·179	0·254	0·285	0·158
5, 6	0·461	0·190	0·357	0·326	0·354
0, 0	0·537	0·584	0·583	0·591	0·557
1, 1	0·304	0·318	0·306	0·381	0·308
2, 2	0·153	0·137	0·110	0·158	0·197
1, 0	0·318	0·274	0·271	0·264	0·329
2, 1	0·279	0·304	0·269	0·255	0·242
3, 2	0·330	0·384	0·345	0·376	0·347
4, 3	0·286	0·408	0·357	0·323	0·310
5, 4	0·417	0·529	0·436	0·411	0·483
2, 0	0·112	0·082	0·049	0·093	0·103
3, 1	0·115	0·116	0·078	0·118	0·138
4, 2	0·197	0·184	0·100	0·183	0·264

pressures. These values have been tabulated in Table IV, to compare with the theoretical maximum transition probabilities. The latter has been derived from potential energy curves, using Morse and Rydberg functions.[12]

TABLE IV.

Most Probable Transitions in C_2 (Swan) System under Different Pressures of Argon.

Theoretical		Experimental				
Morse	Rydberg	10 mm.	15 mm.	20 mm.	25 mm.	30 mm.
			r max. ⟶ *r* max.			
1, 0	1, 0	1, 0	1, 0	1, 0	1, 0	1, 0
2, 1	2, 1	2, 1	2, 1	2, 1	2, 1	2, 1
3, 2	3, 2	3, 2	3, 2	3, 2	3, 2	3, 2
4, 3	4, 3	4, 3	4, 3	4, 3	4, 3	4, 3
5, 4	5, 4	5, 4	5, 4	5, 4	5, 4	5, 4
6, 5	6, 5					
7, 6	7, 5 & 7, 6					
			r min. ⟶ *r* min.			
0, 2	0, 1	0, 1	0, 1	0, 1	0, 1	0, 1
1, 3	1, 2	1, 2	1, 2 & 1, 3	1, 2	1, 2	1, 2 & 1, 3
2, 4	2, 3 & 2, 4	2, 3	2, 3 & 2, 4	2, 3	2, 3	2, 4
3, 6	3, 4 & 3, 5	3, 4	3, 5	3, 4	3, 4 & 3, 5	3, 5
4, 7	4, 6	4, 5	4, 6	4, 5	4, 5 & 4, 6	4, 6
5, 8	5, 7	5, 6	5, 7	5, 6	5, 6 & 5, 7	5, 7

Intensity Centres.—To compare the gross intensity distribution under all the conditions, it was thought desirable to calculate the intensity centres

as shown by Tawde.[8] The values of $\bar{\lambda}$ of intensity centres are given in Table V.

TABLE V.

Positions of "Intensity Centres" C_2 (Swan) System.

Sequence	Pressure of Argon				
	10 mm.	15 mm.	20 mm.	25 mm.	30 mm.
0, 2	6090·14	6047·38	6050·75	6075·36	6066·26
0, 1	5580·36	5569·52	5569·11	5583·66	5587·09
0, 0	5149·42	5140·01	5148·25	5147·80	5147·36
1, 0	4716·30	4706·68	4710·31	4714·13	4714·45
2, 0	4374·07	4373·50	4372·93	4373·81	4373·63
Intensity Centres of the System ..	5119·50	5064·02	5140·81	5123·63	5091·18

Effective Temperatures.— Though one would expect no appreciable change in temperature from one pressure to the other in the order examined here, the evaluation of these is likely to provide an additional data to study the thermal equilibrium. On the basis of Boltzmann distribution in the initial states, the temperatures have been calculated from vibrational energy. These are given in Table VI.

TABLE VI.

Effective Temperatures.

Pressure ..	10 mm.	15 mm.	20 mm.	25 mm.	30 mm.
Temperature ..	5500° K	7070° K	6280° K	5630° K	6430° K

IV. Discussion.

We have found from the intensities that the Condon distribution holds for all the cases studied here. It is to be noted that this is in agreement with the results of Johnson and Tawde for the case of argon excitation studied by them. However, in respect of the excitation functions $\Sigma I/\nu^4$, the only

case which comes nearer to that of Johnson and Tawde is that of 15 mm. pressure. With this, the statistical weight of the system is 523, the maximum and the only value, nearer to 644 of Johnson and Tawde. One may notice that for this pressure, in comparison to others, the probabilities are unusually strong for the (1, 0) and (0, 2) sequences. But of these the selectivity of (0, 2) sequence has already been noted by Johnson and Tawde.[4]

It can be seen from the following graphs of Figs. 1 and 1 (*a*), that the intensity distribution in the Swan system as excited in argon gas, has some anomalous features. The graphs show the value of log I/ν^4 of a band in each sequence against the value of $E_{v'}$. In every case of argon pressure

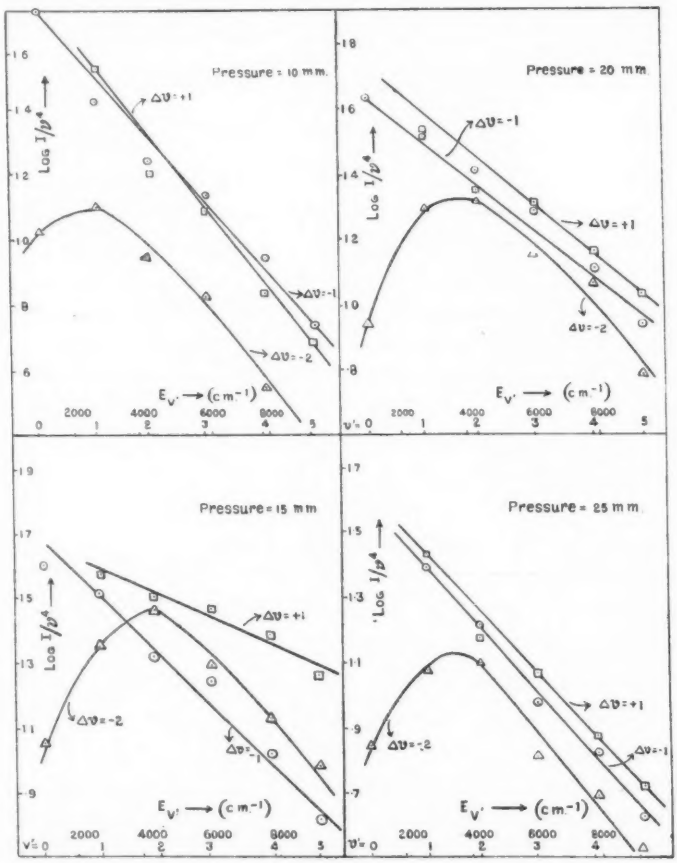

FIG. 1.

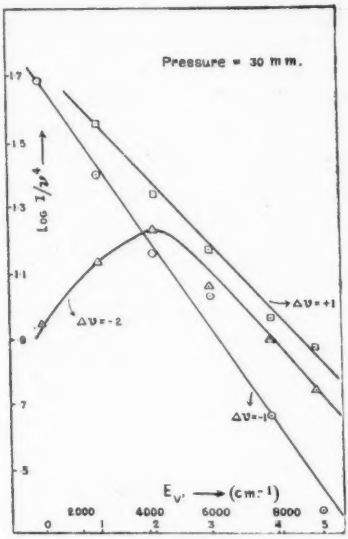

FIG. 1 (*a*).

that is studied, the sequence with $\Delta v = -2$ shows a relation which is not a straight line; for all other sequences, the graph is more or less a straight line under all conditions. This sequence, as we have noted above, is the one which comes out selectively under the transition probabilities.

It can very well be concluded from the experimental values of Table IV, that the pressure of argon seems to exert practically no effect on the locus of maximum transition probabilities. Comparing, however, these probabilities with the theoretical values, we find that the experimental results are very well agreeable to the theoretical values calculated from the Morse's and Rydberg's potential energy expressions in the region of $r_{max.} \rightarrow r_{max.}$. In the region of $r_{min.} \rightarrow r_{min.}$, Rydberg's potential energy expression gives much better agreement than Morse's, a result in agreement with the conclusions of Johnson and Dunstan[3] and of Tawde[11] on BeO and N_2 (second positive) systems respectively.

It will be remembered that $\Sigma\, I/\nu^4$ has been termed as the excitation function which is proportional to the number of molecules in the initial vibrational states. Examination of the same for initial electronic states of the C_2 molecule (Swan system), shows that the change of pressure of the argon gas in the discharge tube does change the excitation function. The change is more marked as we go from lower vibrational states to

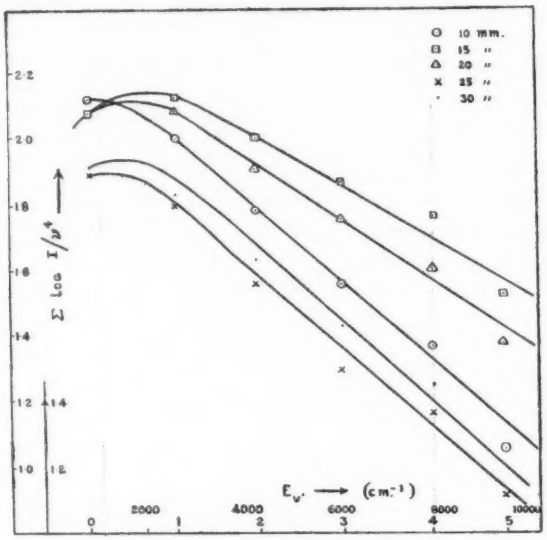

FIG. 2.

higher ones as can be noticed from the nature of the graphs of Fig. 2. It means that the population of molecules in the higher vibrational levels are more sensitive to changes in the argon pressure. This may be a likely consequence of the greater stability of the first few levels in the excited state, the life period of the molecules within these being higher. To interpret in terms of the collisions of the second kind which we shall discuss in the next paragraph, it seems tempting to assume that a few of the molecules possessing lower vibrational quanta will be able to take energy from the excited argon atoms and turn into molecules of higher vibrational energy and thus cause a relatively large change in the already small populations of the higher states. The relative change thus noticed in the lower states will be comparatively small owing to large populations there. This may be similar to the effect found by Duffendack, Revans and Roy[9] in N_2^+ bands where the energy is spread out towards the higher vibration states when the bands are excited by collisions of the second kind with metastable helium.

Production of C_2 (Swan) System in the Presence of Argon.—As to the manner in which C_2 (Swan) system is excited in the presence of argon it may be mentioned that the explanation given below will be, more or less of a speculative nature, on account of the absence of any accurate knowledge of the energy changes going on in the discharge tube.

In the present case, the discharge tube, as pointed out before, contained one carbon electrode and one aluminium electrode and the Swan bands appeared only in a small portion of the capillary nearer the carbon electrode. The minimum pressure of argon necessary for this has been evaluated from the intensity values of the (0, 0) sequence and by drawing a graph of intensity-slopes against argon pressures. From this observation, we have concluded and have reason to believe that for the appearance of (0, 0) band which is the strongest, a minimum pressure of 2 to 3 mm. is necessary and this is sufficiently high for the purposes of explanation that we shall attempt to offer on the basis of Klein and Rosseland's theory of inelastic collisions of the second kind.[13]

Duffendack and Fox[5] have found from experiments that the CO bands can be excited in a discharge tube containing CO gas by direct electron impacts. Duffendack and Smith[6] showed that in the CO—inert gas mixtures, especially He-CO, the process of direct electron impact is not operative, but they consider the possibility of simultaneous excitation and ionization of CO by excited He and Ne atoms by collisions of the second kind. In view of these contentions we might postulate as follows: If for instance, we assume the energy of the excited argon atoms to be transferred over to CO by collisions of the second kind, we might expect the dissociation of the latter to C and O atoms in their ground-state and the subsequent formation and excitation of the C_2 molecule to emit Swan bands. Carbon being continuously reinforced from carbon electrodes and oxygen being present only as an impurity so as to be a negligible factor in the resultant spectrum, such a process might be said to be highly probable. The only quantitative evidence that we can bring to bear on this view is the energy of the excited argon atoms. These atoms carry various quanta of energy up to a limit of 15·69 electron-volts which is the ionisation potential of argon. This being much in excess of the dissociation energy (about 10 e-volts) of CO, will be able to dissociate it as above, leaving a surplus of less than 5·69 electron-volts, which the argon atoms carry to excite the molecular Swan spectrum of carbon (the potential required being 2·4 e-volts). The possibility of this can be demonstrated, if we imagine that before the introduction of the rare gas atoms in the discharge, the entire spectrum is due to Angstrom bands of carbon monoxide, the presence of CO being due to the slight impurity of oxygen left in the discharge tube and invariably such is the case in every experiment in which the discharge tube spectra are examined, even though the tube is exhausted to a tolerably low limit of vacuum. In the present case, owing to one electrode being carbon, after the dissociation of CO, it is only the carbon that preponderates and

it is this fact that will bring about the formation of C_2 molecules and their excitation into Swan system as indicated above after the introduction of the high pressure argon. Further support is lent to this by the observation that the Swan bands do not appear all along the capillary but near that end of the capillary where the carbon electrode is fixed. The appearance of the system is strong for a distance of about $1\frac{1}{2}$ inches of the capillary after which it gradually fades. The bands disappeared entirely after a distance of about 4 inches. This may be due to the number of carbon molecules gradually diminishing as we go away from the carbon electrode. In order to test this further, we substituted the aluminium electrode by the carbon so that both the electrodes were similar. Under these circumstances, we found that the original Angstrom bands were replaced in the capillary by Swan bands after the introduction of the argon gas; but they were strong only at two ends of the capillary. This observation lends further support to the contention that it is the dissociation of carbon monoxide into carbon in an excess, that brings about the appearance of C_2 Swan system and only the collisions of the second kind with rare gas atoms are responsible for bringing this about. After running the discharge tube for a long time and then cutting off the discharge, the tube continues to glow pale white for some time which might resemble the afterglow spectrum of some oxide of carbon.

Examination of temperatures shows that in none of the cases studied, the temperature equilibrium is reached. It is therefore difficult to ascribe a true temperature from the vibrational energy to the Swan system as excited in the present experiments. This non-existence of true temperature can be explained on the basis of general rules given by Oldenberg[7] for determining the true temperatures. According to him a true temperature is indicated in the case of emission spectra excited by electrical discharge at high pressure of added rare gas, if the molecules have a good chance to come to thermal equilibrium during the life-time of the excited state. It is possible in this case that during the life-time of the excited state, the vibrational energy is completely changed due to collisions with excited rare gas atoms. Such is not the case, however, with the rotational energy which is not appreciably changed. In this connection, we can point out the evidence of Duffendack, Revans and Roy[9] who have shown that when N_2^+ bands are excited by impacts of second kind in gas-mixtures, no change in rotational energy occurs. In cases like these, the existence of true rotation temperature as shown by many authors and non-existence of true vibration temperature as found in the present experiments may be a consequence of Oldenberg's rules.

The study of intensity shifts with pressure does not reveal any marked regularity. The wave-length of intensity centres in sequences does not appreciably change as we pass from one pressure to the other. But the intensity centre for the whole system has definite shift towards more refrangible side and occurs at the pressure of 15 mm. of argon. This minimum wave-length coincides with the highest temperature recorded for this pressure within the limits examined, as seen from the following graphs of Figs. 3 and 3 (*a*). In the absence of any knowledge of

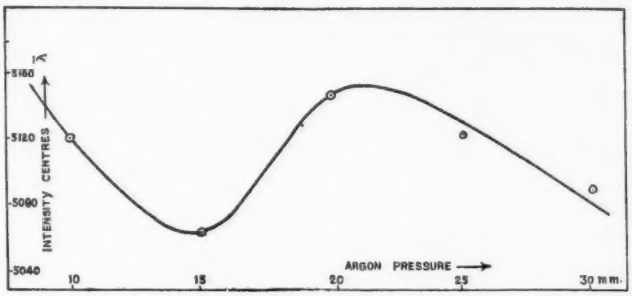

FIG. 3.

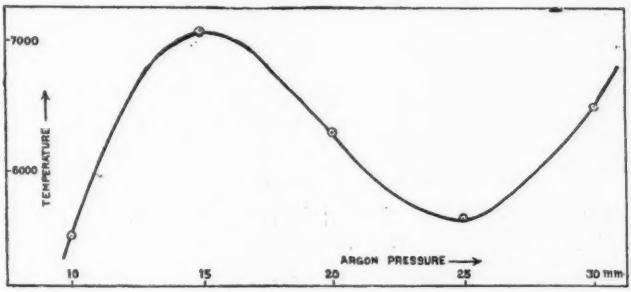

FIG. 3 (*a*).

true temperatures existing within the tube, it is impossible to say whether the highest limit of temperature occurs near about this pressure.

It is interesting to add two more relations here, which resemble the nature of graphs, referred to above. They pertain to maxima of the (0, 2) sequence [*cf.* Fig. 1 and 1 (*a*)] and the variation of the statistical weights of the system with pressure [*cf.* Table II (*a*)]. The first relation is the position of maximum of 0, 2 sequence on the E_v', scale and its shift with pressure. This is shown below in Fig. 4. The second relation, namely the variation of $\Sigma I/\nu^4$ is plotted below, in Fig. 4 (*a*). The graphical relations of Figs. 3 (*a*), 4 and 4 (*a*) resemble each other and the special cases to which they refer require elucidation from theoretical standpoint.

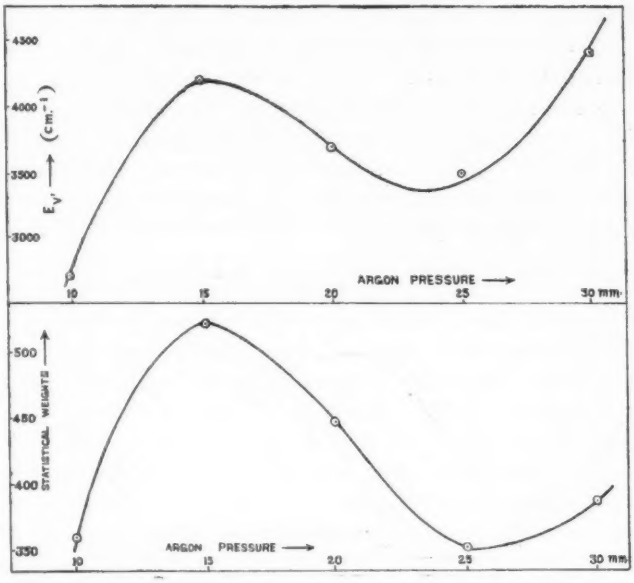

FIG. 4.

FIG. 4 (*a*).

The authors take great pleasure in expressing their thanks to the authorities of the Science College, Patna, for allowing the use of their microphotometer and to the Principal, Prof. A. T. Mukherjee, for the hospitality extended to one of us (D.D.D.) during the stay at Patna.

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ON THE EMISSION SPECTRUM OF $SiBr_4$.

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(From the Department of Physics, Muslim University, Aligarh.)

Received September 23, 1937.

Introduction.

Miescher[1] has recently studied the spectrum of $SiBr_4$ and has obtained a number of bands all degraded towards shorter waves. He has given an analysis for these bands, which has been confirmed by Bashford, Briscoe and Jevons.[2] We have studied the spectrum of $SiBr_4$ under different conditions of the flowing vapour and with condensed and uncondensed discharge. The results obtained are described below, and it is shown that the nature of the spectrum undergoes certain radical changes under varying conditions of the flowing vapour.

Experimental.

A discharge tube of the H pattern with the usual side bulbs containing P_2O_5 and crushed NaOH and fitted with a quartz window has been used. The substance was contained in another side bulb with a stop-cock for the regulation of the flow of the vapour. The discharge tube was provided with nickel electrodes and was connected to a high vacuum apparatus, operated by a mercury diffusion pump which was backed by a rotary oil pump. The flow of the vapour was adjusted to give the desired pressure by having two stop-cocks on either side of the discharge tube. Pressures were measured on a Macleod gauge. The tubes were run on a quarter K. W. transformer delivering 15,000 volts. For condensed discharge a set of three ordinary Leyden jars arranged in parallel was used with a spark gap of about 2 mm. in series with the tube. Medium Hilger quartz spectrograph has been used to photograph the spectrum in the ultra-violet region. The plates have been measured on an Abbe Comparator, using Cu arc lines as standards. The wave-lengths of the beginning, maximum and end of the continuous emission bands have been determined from microphotometer records, which were obtained on a Zeiss recording microphotometer.

Description of the Spectrum.

With pressures higher than 0·5 mm. of Hg, under both conditions of discharge, the spectrum consists of only a number of continuous emission bands, the details of which are given in Table I. No discrete bands were

TABLE I.

Long wave-length limit A.U.	Maxima A.U.	Short wave-length limit A.U.
5850	4220	3750
3640	3570	3470
3470	3435	3415
3415	3345	3250
3160	3120	3040
3000	2910	2835
2835	2780—2710 (Broad)	2680
2665	2640—2630 ,,	2600
2425	2420	2400
	2370 ?	

observed. When the pressure of the flowing vapour was reduced to 0·2 mm. of Hg, all the continuous emission bands, except the one at λ 4220 disappeared, giving rise to a system of bands degraded towards shorter waves. These bands have been identified as the bands due to SiBr.[1,2] At a presssure of 0·05 mm. of Hg, a number of bands degraded towards the longer waves, in addition to those degraded towards shorter waves were observed. At this pressure the continuous emission bands were much reduced in intensity and a set of narrow bands between λ 3700 and λ 3930 in the body of the continuum, similar in structure to the group A bands observed in the experiments with $SiCl_4$,[3] were observed. These, however, were too faint to be measured. In analogy with other molecules $SiCl_2$ and $SnCl_2$ discussed elsewhere,[3] we tentatively suggest that these narrow bands might be due to a triatomic molecule $SiBr_2$. Fig. 1 is a reproduction of the plate which shows all the bands but on which these narrow bands are not clearly visible.

The region between λλ 3350 and 2700 consists of a large number of bands some of which are degraded towards the shorter waves and the rest towards the longer waves. The wave-lengths of the SiBr bands degraded

towards the shorter waves are given in Table II, together with the measurements of Miescher.* One extra band at λ 3208·2 not observed by Miescher

TABLE II.

Bands degraded towards the Shorter Waves.

Meischer λ in A.U.	Here λ in A.U.	Meischer λ in A.U.	Here λ in A.U.
3233·6	..	3057·6	..
3217·4	..	3047·5	3047·1
..	3208·2	3033·4	3033·2
3192·0	3191·9	3008·8	3008·8
3176·3	3175·2	2995·0	2995·6
3167·5	3166·6	2982·3	..
3151·7	..	2971·2	2971·2
3136·0	3135·3	2958·3	2958·3
3126·6	3126·0	2945·7	..
3111·3	3111·4	2921·8	2922·0
3096·7	..	2910·3	..
3086·9	3086·3	2874·9	..
3072·2	3071·9		

fits into his analysis in the position (0—6). The wave-lengths of the bands degraded towards longer waves are given in Table III. The bands between λλ 2862 and 3170 lie in the region covered by Miescher's bands and most of them are confused in the structure of the latter bands.

* These bands have been measured more recently by Jevons and Bashford (*Proc. Phys. Soc. Lond.*, 1937, **49**, 554) under higher dispersion. They show that the final level of these bands which is presumably the ground state of SiBr is not a singlet state as previous data indicated but a $^2\Pi$ state with an electronic separation of the expected order of magnitude.

TABLE III.

Bands degraded towards Longer Waves.

λ Air A.U.	Int.	ν in Vac. cm.$^{-1}$	Classification $v' - v''$	
3320	(2)	30112	2—5	Group B.
3297	(1)	30322	1—4	
3274	(0)	30535	0—3	
3267	(2)	30600	2—4	
3245	(3)	30808	1—3	
3222	(5)	31028	0—2	
3198 ?				
3170·4	(4)	31533	0—1	
3150·6	(6)	31731		
3058 ?	(0) ?	32692		
2990·6	(0)	33428		
2965·9	(8)	33707		
2926·5	(4)	34161		
2872·3	(?)	34805		
2862·5	(3)	34924	0—3	Group A.
2842·4	(0)	35171	1—3	
2822·7	(6)	35417	0—2	
2783·3	(6)	35918	0—1	
2764·2	(6)	36166	1—1	
2745·2	(6)	36417	0—0	
2727·7	(2)	36650	1—0	
2708·9	(2)	36904	2—0	

(Figures in brackets in Column 2 indicate visually estimated intensities.)

Analysis of the Bands degraded towards Longer Waves.

At first these bands were suspected to be due to the SiO molecule[4] which shows an extended band system degraded towards longer waves in the region λλ 2176—2925. A comparison of the wave-lengths of the bands shows, however, that this is not so. The SiO bands have not been obtained in these investigations either on $SiCl_4$ or $SiBr_4$ plates. The bands between λλ 2708·9 and 2842·4 (Group A) as well as bands between λλ 3198 and 3320 (Group B) are free from the confusion with Miescher's bands of SiBr. On account of the confusion of the intermediate bands it has not been possible to arrive at a satisfactory analysis of all the bands. But a tentative analysis of the two groups of the bands which are free from the confusion is given below in Tables IV and V.

TABLE IV.

Group A Bands.

v' \ v''	0		1		2		3
0	36417	499	35918	501	35417	493	34924
	(233)		(248)				(247)
1	36650	484	36166				35171
	(254)						
2	36904						

TABLE V.

Group B Bands.

v' \ v''	1		2		3		4		5
0	31533	505	31028	493	30535				
					(273)				
1					30808	486	30322		
							(278)		
2							30600	488	30112

The analysis as it is, does not include the bands at λλ 3150·6, 2990·6, 2965·9 and 2926·5, which are among the confused bands. The analysis indicates that the bands belong to two electronic systems, both having the same final state, with a frequency of about 500 cm.$^{-1}$ The frequency of the excited state of the group A bands is about 250 cm.$^{-1}$, while that of group B bands is about 275 cm.$^{-1}$ None of these frequencies corresponds to the two known frequencies of SiBr, *viz.*, $\omega'' = 423{\cdot}3$ cm.$^{-1}$ and $\omega' = 574{\cdot}0$ cm.$^{-1}$ The magnitude of the frequencies, however, are such as could be expected for the SiBr molecule. While considerations of experimental conditions, as well as comparison with known data rule out the possibility of SiO as the emitter of these bands, the absence of a common level between these bands and the already known bands of SiBr renders the attribution of these bands to the emitter SiBr tentative. The only possible emitter other than SiBr which suggests itself to us is $SiBr^+$.

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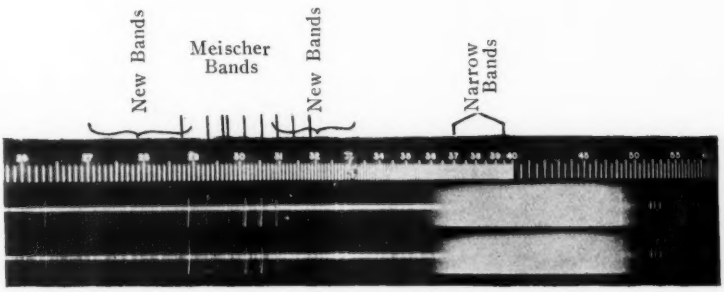


FIG. 1.

HETEROCYCLIC COMPOUNDS.

Part V. Synthesis of 2-Methyl-6-ethyl-7-hydroxy-chromone and Its Derivatives.

By R. D. Desai and Sheikh Abdul Hamid.

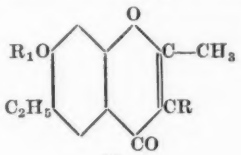
(*From the Department of Chemistry, Muslim University, Aligarh.*)

Received September 23, 1937.

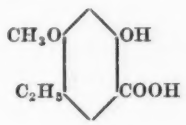
(Communicated by Dr. R. K. Asundi, M.Sc., Ph.D.)

The vigorous acylation of *o*-hydroxy-acetophenones[1] provides a useful method for the synthesis of chromones containing substituents in various positions, and this method has been subjected to a critical investigation by various investigators[2] to determine the factors leading to the formation of coumarins and chromones. Robinson and co-workers[3] have utilised this method to synthesise the naturally occurring flavones and flavonols. The only attempt to utilise the Kostanecki Reaction for the synthesis of chromones containing alkyl groups in the benzene nucleus is that of Wittig, Baugert, and Richter[4] who acetylated 2-aceto-4-methyl-, 2-aceto-6-methyl-, 2-aceto-5-methyl-, and 2-aceto-3 : 5-dimethyl-phenols. These types of flavones, flavanones and flavonols derive additional interest from the fact that matteucinol,[5] as well as another colouring matter isolated from *Matteucia orientalis* are flavanones containing dimethylated benzene nucleus.

The present communication deals with the application of the Kostanecki Reaction to 2 : 4-dihydroxy-5-ethylacetophenone which readily gave 7-acetoxy-6-ethyl-3-acetyl-2-methylchromone (I, $R = R_1 = CH_3 - CO$) with acetic-anhydride in the presence of anhydrous sodium acetate, while 7-hydroxy-6-ethyl-2-methylchromone (I, $R = R_1 = H$) was obtained from it by the usual method. Dilute alkali hydrolysed this chromone to 2 : 4-dihydroxy-5-ethylacetophenone, but 2-hydroxy-4-methoxy-5-ethylbenzoic acid (II) was obtained by the hydrolysis of its methyl ether (I, $R = H$, $R_1 = CH_3$). This acid was also obtained by the action of potassium bicarbonate on 4-ethylresorcinol[6] and subsequent methylation. The chromone structure of (I) is thus proved beyond doubt.



(I)



(II)

We are busy synthesising the flavones and flavonols from this as well as similarly related ketones.

Experimental.

7-Acetoxy-6-ethyl-3-acetyl-2-methylchromone.—A mixture of 2 : 4-dihydroxy-5-ethylacetophenone (10 g.), anhydrous sodium acetate (20 g.) and acetic anhydride (50 c.c.) was heated in an oil-bath at 170–180° for ten hours. The solid obtained by pouring the contents into water was collected, and crystallised from dilute alcohol when long, silky needles melting at 138°, were obtained (5 g.). [Found : C, 66·4 ; H, 5·7 ; $C_{16}H_{16}O_5$ requires C, 66·6 ; H, 5·6 per cent.]

The alcoholic mother-liquor furnished more of the same compound after removal of the solvent, and extraction of the original ketone with dilute alkali from the ethereal solution of the residue. *7-Hydroxy-6-ethyl-3-acetyl-2-methylchromone* was obtained by shaking the acetoxy derivative with dilute ammonia for one hour, and acidifying the filtered solution with concentrated hydrochloric acid. It crystallised from dilute alcohol in thick, rhombic plates (m.p. 193°). [Found : C, 68·0 ; H, 5·8 ; $C_{14}H_{14}O_4$ requires C, 68·3 ; H, 5·7 per cent.]

Its alcoholic solution gave no coloration with ferric chloride, and dissolved in concentrated sulphuric acid with a yellow colour. *The methylether*, obtained by methylating its solution in alkali with dimethyl sulphate crystallised from hexane in plates (m.p. 158°). [Found : C, 69·0 ; H, 6·3 ; $C_{15}H_{16}O_4$ requires C, 69·2 ; H, 6·2 per cent.]

7-Hydroxy-6-ethyl-2-methylchromone was obtained by heating the solution of the chromone (1·5 g.) in 5 per cent. sodium carbonate (20 c.c.) for one hour on a sand-bath under reflux. The chromone obtained by acidifying the filtered alkaline solution crystallised from dilute alcohol in rhombic plates (m.p. 204°). [Found : C, 70·5 ; H, 6·1 ; $C_{12}H_{12}O_3$ requires C, 70·6 ; H, 5·9 per cent.]

The chromone dissolved in concentrated sulphuric acid with a yellow colour and its alcoholic solution did not give any coloration with ferric chloride.

The methylether obtained in the usual manner with dimethyl sulphate crystallised from hexane in plates (m.p. 90°). [Found : C, 71·3 ; H, 6·5 ; $C_{13}H_{14}O_3$ requires C, 71·6 ; H, 6·4 per cent.]

The acetyl derivative obtained by heating the chromone (0·5 g.) with acetic anhydride (3 c.c.) and a few drops of pyridine crystallised from dilute alcohol in fine needles (m.p. 99°). [Found : C, 68·1 ; H, 5·9 ; $C_{14}H_{14}O_4$ requires C, 68·3 ; H, 5·7 per cent.]

Hydrolysis of 7-hydroxy-6-ethyl-2-methylchromone with alkali and formation of 2 : 4-dihydroxy-5-ethyl-acetophenone.—The solution of the chromone (0·5 g.) in normal caustic soda solution (10 c.c.) was heated on a sand-bath under reflux for two hours. The cooled solution was diluted with water, filtered and acidified with concentrated HCl. The solid thus obtained was dried and crystallised from benzene when flat plates (m.p. 118°) were obtained. This was identified as 2 : 4-dihydroxy-5-ethylacetophenone by comparison with an authentic specimen.

Hydrolysis of 7-methoxy-6-ethyl-2-methylchromone with alkali and formation of 5-ethyl-4-methoxy-2-hydroxybenzoic acid.—A suspension of the methyl-ether (0·5 g.) in normal caustic soda solution (10 c.c.) was heated on a sand-bath under reflux for two hours. The solid obtained by acidifying the cooled solution with dilute HCl and purified through sodium bicarbonate, crystallised from dilute alcohol in thick, prismatic needles (m.p. 192°). [Found : C, 61·3 ; H, 6·2 ; $C_{10}H_{12}O_4$ requires C, 61·2 ; H, 6·1 per cent.]

Its aqueous solution gave violet coloration with ferric chloride, while the alcoholic solution gave bluish black colour with the same reagent.

2 : 4-*Dimethoxy-5-ethylbenzoic acid was obtained* by methylating the acid (0·5 g.) with three lots of dimethyl sulphate (2 c.c.) each and warming on the water-bath for half an hour. After purification through sodium bicarbonate, it crystallised from dilute alcohol in plates (m.p. 126°). Its alcoholic solution did not give any coloration with ferric chloride. [Found : C, 62·7 ; H, 6·7 ; $C_{11}H_{14}O_4$ requires C, 62·9 ; H, 6·7 per cent.]

Synthesis of 2 : 4-dihydroxy-5-ethylbenzoic acid.—We are indebted to Dr. R. C. Shah of the Royal Institute of Science, Bombay, for the detailed information regarding this preparation (Unpublished work).

A solution of 4-ethyl-resorcinol (5 g.) in anhydrous potassium bicarbonate (25 g.) and water (50 c.c.) was heated on a sand-bath for two hours. The cooled solution was diluted with water, filtered and acidified with concentrated HCl. The acid crystallised from hot water in silky needles (m.p. 188°) (yield 70 per cent.). [Found : C, 59·1 ; H, 5·6 ; $C_9H_{10}O_4$ requires C, 59·3 ; H, 5·5 per cent.]

Its aqueous solution gave bluish black coloration with ferric chloride.

Synthesis of 5-ethyl-4-methoxy-2-hydroxybenzoic acid.—The above dihydroxy acid (1 g.) was dissolved in normal alkali (10 c.c.) and dimethyl sulphate (3 c.c.) was gradually added with constant shaking. After half an hour, the acid was obtained by acidification with dilute HCl, and crystallised from dilute alcohol when thick, prismatic needles (m.p. 192°) were obtained. The melting point was not depressed by admixture with

the specimen obtained by the alkaline hydrolysis of 7-methoxy-6-ethyl-2-methylchromone. Further methylation of this acid gave the dimethoxy acid (m.p. 126°), identical with the specimen prepared from the chromone.

Summary.

7-Acetoxy-6-ethyl-3-acetyl-2-methylchromone has been prepared by the application of the Kostanecki Reaction to 2 : 4-dihydroxy-5-ethylacetophenone. The various derivatives of this chromone have been also described.

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ON A TRIGONOMETRIC SUM.

By S. Chowla.
(*From the Government College, Lahore.*)

Received October 6, 1937.

Theorem : *If* p *runs through all primes, then*

$$\Sigma \frac{1}{p} e^{2\pi i p\phi}$$

is convergent whenever the simple continued fraction for the irrational number ϕ *has bounded partial quotients.*

Proof. Vinogradow (*Recueil Mathématique*, 1937) proved the

Lemma. Let $h > 3$ *be fixed* ; $n = \log N$;

$$\alpha = \frac{a}{q} + \frac{\theta}{qw}, \quad |\theta| \leqslant 1, \ (a, q) = 1,$$

$$n^{3h} \leqslant q \leqslant w, \ w = N n^{-3h} \text{ ; then}$$

$$\sum_{p \leqslant N} e^{2\pi i \alpha p} = O(N n^{2-h})$$

where the constant implied in the O *is an absolute constant.*

Since the simple continued fraction for ϕ has bounded partial quotients, it follows that we can find A, independent of m, such that

$$q_{m+1} < A q_m \tag{1}$$

for all m ; here $\frac{p_m}{q_m}$ denotes the mth convergent to the S.C.F. for ϕ. Now we can find a unique m such that

$$q_m \leqslant w < q_{m+1} \tag{2}$$

for $N > N_0$. For this m we have in virtue of (1) and (2),

$$\frac{w}{A} \leqslant q_m \leqslant w. \tag{3}$$

Further for $N > N_0$,

$$n^{3h} < \frac{w}{A}. \tag{4}$$

From (2), (3), (4) it follows that for the m so determined, we have

$$n^{3h} < q_m \leqslant w. \tag{5}$$

Again we have

$$\phi = \frac{p_m}{q_m} + \frac{\lambda}{q_m\, q_{m+1}} \quad [|\lambda| < 1]$$

$$= \frac{p_m}{q_m} + \frac{\theta}{q_m\, w} \quad [|\theta| < 1] \tag{6}$$

in virtue of (2). From (5) and (6), $a = \phi$, $a = p_m$, $q = q_m$ satisfy the lemma.

Hence putting $h = 4$ in our lemma, we get

$$\sum_{p \leqslant N} e^{2\pi i p\phi} = O\left(\frac{N}{\log^2 N}\right). \tag{7}$$

Hence our result.

It is easy to prove other similar results, *e.g.*, that

$$\sum_{p} \frac{1}{p}\, e^{2\pi i p\phi}$$

converges if ϕ is an algebraic irrational.

PHOTODECOMPOSITION AND ABSORPTION SPECTRUM OF POTASSIUM PERMANGANATE.

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Received November 17, 1937.
(Communicated by Prof. B. Venkatesachar, M.A., F.Inst.P.)

In recent years much valuable work has been done on absorption spectra and photo-dissociation of organic and inorganic molecules, particularly the halides. The study of absorption spectra has many objects. From experimental facts concerning light absorption in the visible and ultra-violet regions, the continuous absorptions observed are correlated with photo-dissociation processes which lead us to chemical data such as interatomic distances and electronic configurations of the molecules.

It is known that potassium permanganate is decomposed photo-chemically. Pougnet[1] found that in the presence of oxalic acid potassium permanganate is light sensitive, reduction taking place to potassium manganate. Mathews and Deway[2] noticed a slight decomposition when a strong solution of potassium permanganate is illuminated by light from quartz mercury vapour lamp. But no experiments were made by these to obtain any quantitative data on the decomposition.

The work of Rideal and Norrish[3] appears to be the only one in which an effort has been made to study the photo-chemical effect in relation to the absorption spectrum and their results were published in two important papers. They, however, based their calculations on the assumption that the only photo-active line in the quartz mercury arc spectrum is 3128 Å and that the co-efficient of absorption for the green and yellow light is the same as for ultra-violet light. They recognised at the same time that until some means are found of discriminating between the photo-activity of the lines 3650, 3128 and 2536 Å given by the mercury vapour lamp, no definite assertion can be made as to the number of light quanta concerned in the decomposition of the Mn ion. It is known that the Mn ion on illumination is decomposed photo-chemically according to the equation

$$KMnO_4 \rightleftharpoons K^{\circ} + MnO_4'$$

$$MnO_4 + h\nu = MnO_2 + 2\,O'' + O$$

The manganese dioxide becomes hydrated and interacts with caustic potash produced and forms the insoluble potassium manganate according to the equation

$$2\ KMnO_4 = K_2O \cdot 2\ MnO_2 + 3\ O.$$

The selective absorption of potassium permanganate in water has been studied by a number of observers, chiefly for the purpose of general comparison of the absorption bands, notable among them being Formanek,[4] Merton,[5] Hagenbach and Percy,[6] and more recently Vis and Simchen[7]. Recently, an accurate investigation by Lange and Schuster[8] has shown the existence of only five bands, 566mμ, 546mμ, 526mμ, 508mμ and 490mμ. Most of these authors confined their study to absorption in the visible region. The results obtained are not, however, completely concordant, there being no general agreement either in the number of bands or in their positions. Merton and Hartley have recorded only three bands while Hagenbach and Percy observed six bands. But Gombos,[9] Lange and Schuster doubted the existence of one of these bands. The ultra-violet region is most lacking in data, the existing data on light absorption in this region being fragmentary. No quantitative data are available in the literature regarding the absorption in this region. From the few investigations that have been made, even the limits of absorption are not certain. It is with absorption in this region that photochemical considerations are usually concerned, the frequencies associated with it, corresponding to transition between the lower electronic states of the molecules. In view of the discrepancies between the results obtained by different workers and in view of the variation in position of some of these bands under different conditions, the author has examined the absorption spectrum and photo-chemistry of potassium permanganate. The present paper deals primarily with a study of the absorption spectrum and photo-decomposition in monochromatic light.

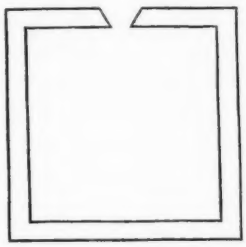
Experimental.

For the spectral measurements, two instruments were used; a Hilger E_2 quartz spectrograph covering the region 4000 — 2000 Å and of dispersion 16 Å/mm. at 3000 Å and 8 Å/mm. at 2500 Å and a glass Littrow spectrograph with an extra dense flint glass prism, covering the region 9000 Å — 4000 Å giving a dispersion of 9 Å and 4500 Å.

And as source of light, a condensed spark between Zn-Cd and Sn-Pb electrodes was used for the ultra-violet and a 500 watt projector lamp for the visible region.

For the ultra-violet and near ultra-violet regions, Imperial Special Rapid and Illford Special Rapid plates were used, while for the visible region,

Eastmann Panchromatic plates and for the infra-red region 6500 Å — 9000 Å Eastmann Infra-red plates were used. As absorption cells, quartz cells varying in thickness from 0·01 mm. to 10 mm. were used in this work. Those from 1 mm. to 10 mm. consist of square plates of glass, bored and ground on both faces. These were closed with plane parallel plates of silica and were held in position by rubber bands. To make those from 0·01 mm. to 1 mm. tinfoil was folded till it was of the required size and thickness when it was cut to the form shown in the sketch. It was then covered



lightly with seccotine and pressed between the two plane parallel plates of quartz. The cell is mounted in a wooden carrier in front of the spectrograph.

The absorption cells are first thoroughly cleansed from organic matter with concentrated chromic acid solution and then washed with distilled water and finally rinsed with N/100 potassium permanganate solution.

For obtaining the absorption spectra, solutions were always freshly prepared by dissolving accurately weighed quantities of Kahlbaum's pure salt in distilled water. The time of exposure and the conditions of running were maintained constant. The plates obtained were examined by visual and photometric methods. The principle of the recording photo-electric microphotometer used for these measurements is, that a narrow beam of light is sent through the movable photographic plate to be studied and focussed on to a photo-electric cell, the intensity of the unabsorbed light being registered by electrometer deflection. The percentage transmission of the solution for a particular λ was determined by reading from the photometric record the deflection of the electrometer. The extinction co-efficient is proportional to the concentration of manganese ion and is defined by

$$a_t = 1/cl.\log I_o/I,$$

where c is the concentration and l is the thickness of the solution. I_0 and I represent the intensities of the incident and transmitted light. The values of the extinction co-efficient were plotted against wave-length and typical curve for the band 2300—2010 Å is shown in Fig. 1, and Plates VIII and IX

show the absorption photographs in the visible and ultra-violet regions and show well the strong absorption in the region 2250 – 2000 Å and discrete structure of the band at 3100 Å.

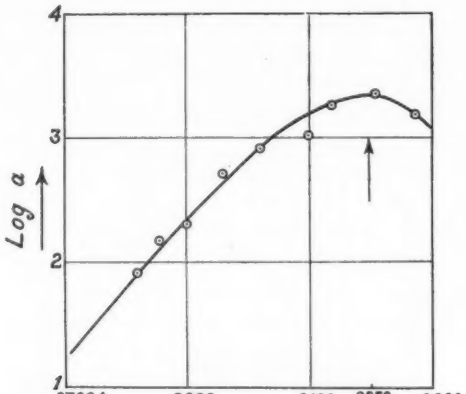


Fig. 1.

In Plate IX the last three spectra in each represent the absorption spectra of N/500 oxalic acid ; N/500 potassium permanganate and of the mixture of equal volumes of these.

It is found that the absorption spectrum consists of three distinct regions, the first extending from red to 4350, the second from 3900 Å to 2750 Å and the third from 2600 Å to 2000 Å. The absorption in the visible region consists of a series of wide and diffuse bands, occurring fairly regularly between 5950–4350 Å, the region of maximum absorption occurring at 5260 Å. The bands in this region did not show any fine structure even at great dilutions. In this region, besides confirming the six bands obtained by Hagenbach and Percy and finding their absorption maxima accurately, a new band at 5920 Å was obtained. I could not find the band at 6350 Å, which has been reported by Vis and Simchen. Fig. 1–A shows the microphotometric trace for the new band at 5920 Å and it will be seen that it is not the result of any contrast effect but is due to real absorption. The percentage of absorption at band centre being 10 per cent. for N/100 solution and for thickness of 1 cm. The absorption maxima of these bands are :—

(*a*) 590 mμ, (*b*) 567 mμ, (*c*) *546* mμ, (*d*) *526·8* mμ, (*e*) 507·8 mμ, (*f*) 489 mμ and 470 mμ.

The second region consists mainly of two bands, one having its maximum at 3535 Å and diffused almost symmetrically on both sides and another strong band with maximum at 3130 Å. With very dilute solutions interesting phenomena are obtained in the ultra-violet region which cannot be studied in stronger solutions. This band showed a discrete structure consisting of about nine diffused bands. The following values were obtained for these :—

λλ 3400 ; 3325 ; 3210 ; 3194 ; 3110 ; 3055 ; 2950 ; 2855 ; 2800 (?).

With concentrated solutions, another band developed at 3925 Å,* which gradually merges with the bands at 3535 Å and 3130 Å till at last the whole region formed one continuous band.

The third or ultra-violet region consisted of two bands with their maxima at 2380 Å and 2050 Å. In the last two cases, the band on the short wave-length side developed to longer wave-lengths with increasing concentration so as eventually to overlap the band on the long wave-length side, giving for N/100, completely continuous absorptions extending from 2900–3700 Å and from 2000–2580 Å. Further investigations of the band 3535 Å are in progress.

It is also interesting to note from the spectrograms that light absorption by a mixture of potassium permanganate and oxalic acid is distinctly greater than that of either separately. This is in agreement with the observations of Dhar and Battacharya[11] who have shown that molecules can react when specially activated, the number of such activated molecules increasing rapidly with light absorption.

The absorption spectra have also been studied at different concentrations. When measured under the photo-electric photometer they showed that the absorption maximum did not change appreciably with increase of concentration, though there was a slight shift towards the red with increasing concentration in the case of the bands at 3100 and 5260 Å. With reduction of concentration, the bands vanish and the long wave-length limit of absorption moves towards the short wave-length side, while with increase of concentration the edge of the band is generally shifted to the long λ side.

Photodecomposition of the aqueous solutions of $KMnO_4$ acidified with sulphuric acid and of mixtures of equal volumes of oxalic acid and potassium permanganate was studied by exposing the solution to the light corresponding to each of the absorption frequencies. In order to obtain approximately monochromatic light, the following method was adopted. The

* Fig. 1–B shows the microphotometric trace for this band.

image of the spark was formed on the slit of the Hilger quartz spectrograph E_2 by means of a quartz lens and the slit was opened out to 1 mm. In the position occupied by the plate holder there was placed a brass plate with a rectangular slot $1'' \times 10''$ alongside which an exit slit measuring $\frac{3}{4}'' \times 1''$ was moved by a screw. Behind this slit was fixed a cell holder made of brass to take the reaction vessel containing the solution. This holder was made hollow to allow a stream of water to pass through it maintaining the temperature constant. The reaction vessel was a rectangular cell of fused silica with plane parallel sides, thickness of the solution being 1 cm. Alongside the rectangular slot in the plate a wave-length scale was fixed which enabled the solution to be exposed to radiation of any wave-length. Rate of decomposition was observed by the bleaching of pink solution as noticed by transmitted light.

In preliminary work the reaction was found to be so critical to the intensity of the exciting radiation and the results obtained were so discordant that it was found that the requirements for steadiness in intensity of the source are very exacting. Owing to the wandering of the spark and the frequent adjustment that it needed the intensity of the exciting radiation was far from constant. And it appeared that an intense and constant source of ultra-violet light should be available before any reliable data are obtained. After several attempts to overcome these defects the author finally used the spark source designed by Hollaender and Foerst.[10] For a detailed description of this, the reader is referred to the original paper. Essentially it consists of two metal discs placed at right angles to each other, the line of their centres being perpendicular to the base. These discs are fastened by means of bakelite shafts to the axes of two old thermograph clocks. Fig. 2 shows the general design. The discs are about 4″ in diameter and make 1 turn in 3 hours. In this experiment the discs were made of Zn-Cd and Sn-Pb. It was found that the arrangement was very satisfactory and that the source of light was constant over a considerable time. During the course of the experiment the variations in the light intensity, were usually of the order 4–5 per cent.

Table I gives the results for a series of experiments and represents the mean of four separate observations.

It is found that there is no strongly selective wave-length and that photo-dissociation takes place whether the solution is illuminated by sunlight, light from iron arc—filtered and unfiltered—or by light corresponding to absorption frequencies. It is found however that the rate of photo-decomposition increases slightly with frequency excitation by radiation of

TABLE I.

Nature of exciting radiation	Time required for bleaching the pink solution
Sunlight	3½ minutes
Fe arc unfiltered	3 „
Fe arc filtered to cut off ultra-violet light	4 „
3750—3450 Å	8 „
3200—2900 Å	5½ „
2600—2350 Å	7 „
2300—2100 Å	5 „

λ 2900–3200 and λ 2250–2000 producing more rapid decomposition than with λ 3750–3400 and λ 2600–2350. At low concentrations the rate of decomposition was proportional to concentration. These results further show that the region of absorption 2250–2000 Å is associated with a relatively high extinction coefficient and is at least as active as the band at 3130 Å. In determinations of quantum yields it is therefore necessary that we should take into consideration this absorption band as well. In view of this fact and the abnormally high extinction coefficient values for the several absorption bands the quantum efficiency should be very much less than unity.

Further experiments are in progress for the determination of the quantum yield and the dependence of the velocity constant on temperature and light intensity.

The author desires to express his thanks to Professor N. R. Dhar for suggesting the problem and for his helpful suggestions and to the Director of the Kodaikanal Observatory for giving necessary facilities and to Professor B. Venkatesachar for his active interest in the work.

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EXPLANATION OF PLATES.

The first spectrum in each case represents the spectrum of the spark source.

In A, B and C the remaining spectra are absorption spectra for increasing concentrations. The second spectrum in C shows the discrete structure of the band at 3130 Å.

In E, 2, 3, 4 represent absorption spectra for increasing concentration. The last three spectra in D and E represent as indicated in the body of the paper, absorption spectra of N/500 oxalic acid, N/500 $KMnO_4$ and of a mixture of the two.

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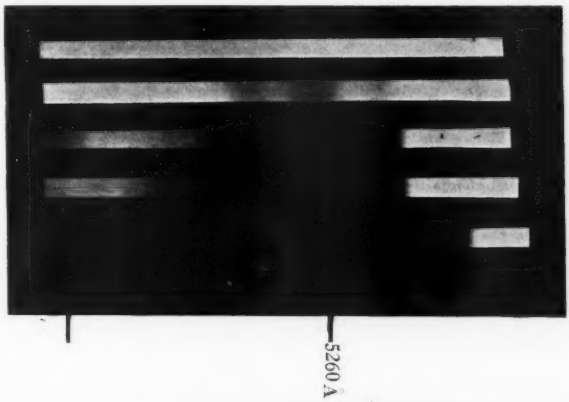
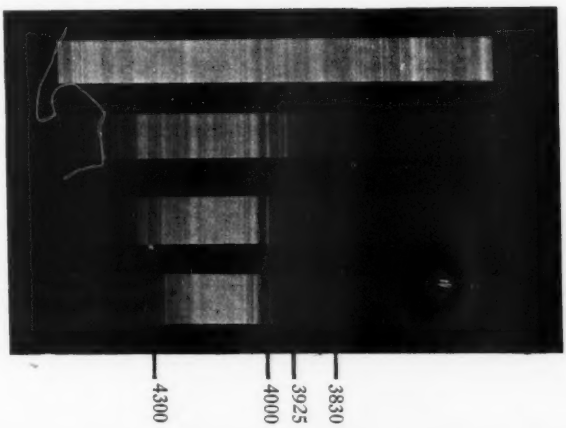
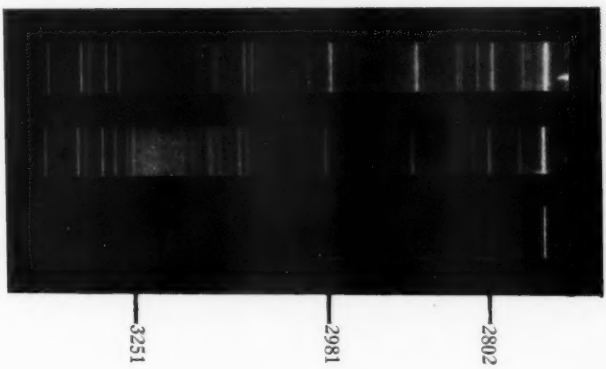
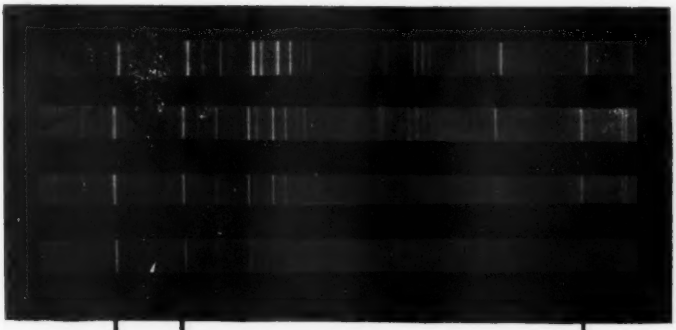

A
Visible
Region
5260 A

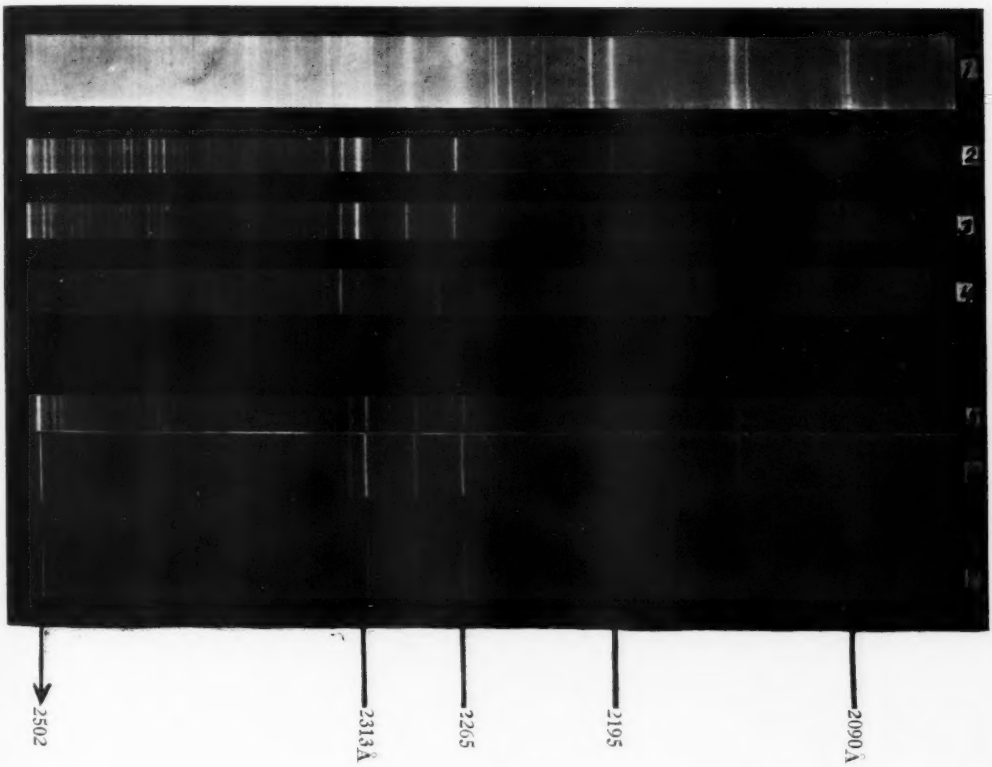

B
Spark
N/100 KMnO4
N/50 „
N/10 „
4300
4000
3925
3830


C
Spark
N/2000 KMnO4
N/100 „
3251
2981
2802

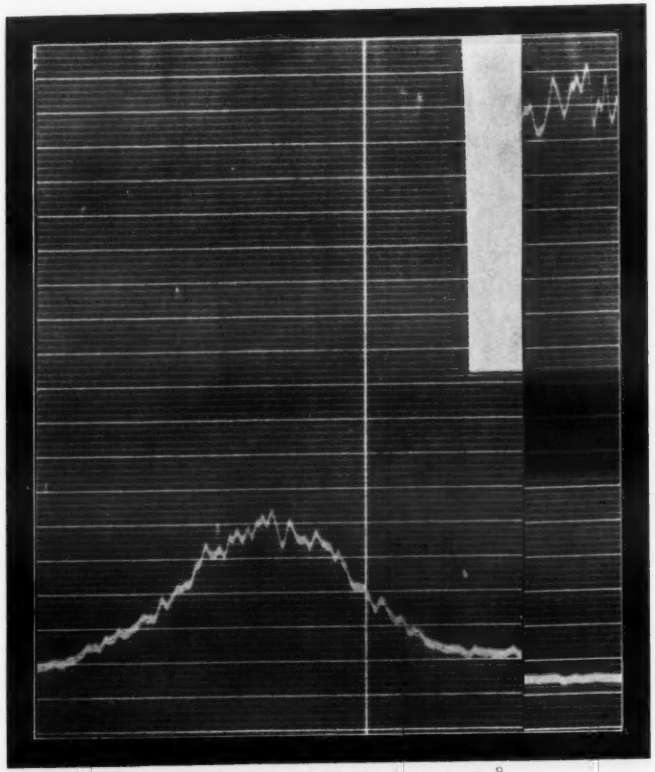
D



E

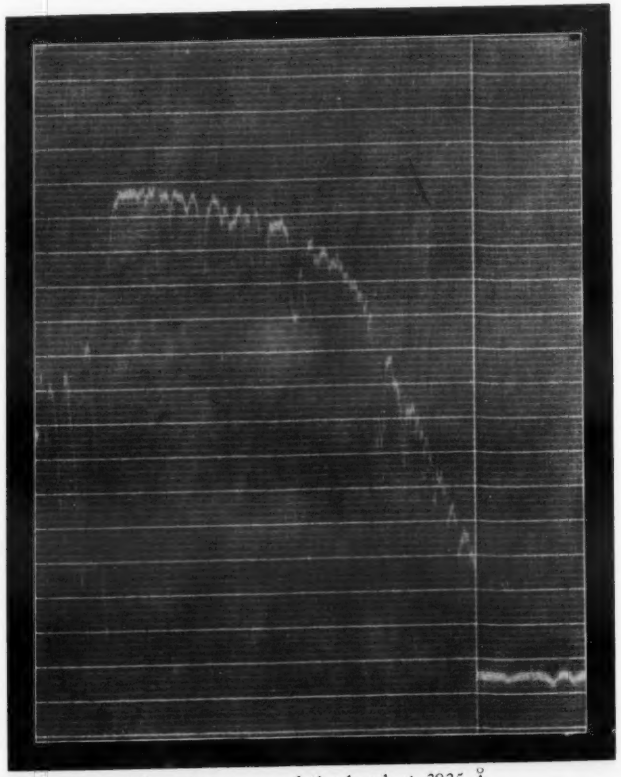


1-A



Microphotogram of the band at 5920 Å.

1-B



Microphotogram of the band at *3925* Å.

FIG. 2. Constant spark source.